N° d'ordre :

THÈSE

présentée

A L'UNIVERSITÉ PARIS-SUD

CENTRE D'ORSAY

pour obtenir

LE GRADE DE DOCTEUR ES-SCIENCES PHYSIQUES

par

DANIEL ESTEVE

MISE EN EVIDENCE PAR RMN D'UN VERRE ORIENTATIONNEL
DANS UN SYSTEME DE QUADRUPOLES EN PRESENCE DE DESORDRE,
LES MELANGES SOLIDES AZOTE-ARGON

Soutenue le 2 FEVRIER 83 devant la Commission d'Examen

J. FRIEDEL	Président
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A Dominique et Jérôme

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I. FRUSTRATION ET DESORDRE (EN MECANIQUE STATISTIQUE)

L'objet de la mécanique statistique est de décrire correctement le comportement d'un système de N particules en interaction sans pour autant résoudre les N équations couplées qui dictent son évolution. On introduit à cet effet des variables macroscopiques comme la pression, l'aimantation ... Cette attitude "réductrice" s'est avérée extrêmement fructueuse. On a pu ainsi élucider le mécanisme des transitions de phase, phénomène par lequel un système à N corps change brutalement de comportement, et cela à une température bien précise. (Le fer a par exemple une aimantation spontanée en dessous de sa température de Curie T_c). Le premier modèle satisfaisant de cette transition a été donné par P. Weiss qui a supposé que l'aimantation moyenne m de l'échantillon obéit à une loi de Langevin dans un champ lui-même proportionnel à m. Cette théorie de champ moyen n'est en fait que qualitativement correcte, et ce n'est que récemment qu'une théorie complètement satisfaisante, incorporant comme degrés de liberté effectifs les fluctuations d'aimantation aux grandes longueurs d'ondes, a été établie. Actuellement, les systèmes présentant une transition de phase de ce type sont bien compris.

Il existe cependant des îlots (ou continents ?) de résistance. L'un des plus intéressants est constitué par les systèmes à la fois frustrés et désordonnés en raison de la réaction "chimique" déclenchée par la réunion de ces deux propriétés réaction qui met en échec les méthodes réductrices de la mécanique statistique dont les succès ont été évoqués ci-dessus.

Les systèmes dilués de quadrupoles en interaction (ou SDQ), dont les mélanges azote-argon sont un exemple, présentent une combinaison originale de frustration et de désordre et font partie de ce groupe. Mais avant de dresser l'inventaire de cette famille, abordons la signification de la frustration et du désordre.

1. FRUSTRATION ET DESORDRE

La frustration

Un système est dit frustré lorsqu'il ne possède pas d'état fondamental satisfaisant simultanément toutes les interactions en présence. Ce concept créé par Toulouse est important car il offre une classification logique des systèmes : le comportement d'un système est d'autant plus pathologique (la

norme étant le système ferromagnétique) que son degré de frustration est élevé.

Considérons par exemple la classe des problèmes de spins sur un réseau. Pour un hamiltonien du type (1) $H = -\sum_{(i,j)} J\, S_i S_j$ $(J>0)$ qui ne donne pas lieu à la frustration, on a une transition du 2ème ordre vers un état ferromagnétique à une température $T_c \approx z\frac{J}{k}$. Lorsque l'hamiltonien est plus complexe et contient des interactions en compétition (exemple : $J_{ij} = J_{jk} = \pm|J|$, $J_{ik} = -|J|$), il n'existe plus de structure satisfaisant simultanément tous les liens. La structure ordonnée qui apparait à basse température est alors le fruit d'un compromis parfois très complexe et la température critique est inférieure à la valeur donnée par la règle simple $kT_c \approx |E_{fond}|$.

Les structures hélimagnétiques sont ainsi un exemple du compromis adopté par la nature pour satisfaire au mieux des interactions en conflit.

L'abaissement de la température critique en comparaison à une situation non frustrée peut se comprendre ainsi : les corrélations qui se développent à $T > T_c$ sont incompatibles avec celles que présentent la structure ordonnée ; à la transition, le système doit choisir de frustrer certains liens et d'inverser une partie des corrélations établies à $T > T_c$. Cet effet peut même aller jusqu'à provoquer un changement de la nature de la transition (passage à une transition du premier ordre) ou à la supprimer complètement (cas du problème Ising $J < 0$ sur réseau triangulaire).

Le désordre

Considérons un système régi par un hamiltonien ferromagnétique du type non frustré (1) dans lequel on supprime aléatoirement certains spins. Le système présente toujours une transition du 2ème ordre mais à une température critique $T_c(X)$ inférieure à $T_c(X=1)$ qui s'annule au seuil de percolation X_c. Le désordre est essentiellement équivalent à une renormalisation des interactions sans modification de la nature de la transition.

Dans le cas d'un système frustré, l'introduction du désordre bouleverse au contraire son comportement thermodynamique.

Frustration et désordre

Une image simple des effets croisés de la frustration et du désordre est fournie par l'analogie suivante. Dans un filet élastique sous tension (≡ frustration), on romp des mailles au hasard (≡ introduction du désordre). On observe d'abord d'importantes modifications du filet, les liens restants tendant à se contracter ; le filet se casse ensuite avant que le seuil de percolation des liens ne soit atteint.

De la même façon, lorsque dans le composé EuS une partie des ions magnétiques d'Europium sont remplacés par des ions non magnétiques de Samarium, la structure ordonnée à longue distance devient instable et une nouvelle phase-dite verre de spin-apparait (Fig.A1).

2. LES SYSTEMES FRUSTRES DESORDONNES

La phase verre de spin (voir l'encart "les verres de spin")

Cette phase est caractérisée par l'existence d'aimantations locales non nulles, sans ordre à longue distance. C'est tout d'abord dans les alliages magnétiques dilués comme Cu Mn (verres de spin canoniques) qu'un tel comportement a été observé. La frustration provient ici du caractère oscillant avec la distance des interactions RKKY. Le label verre de spin a depuis été réclamé pour des matériaux très divers, concentrés ou non, avec des interactions de types différents, mais présentant toujours frustration et désordre.

Le problème de la transition verre de spin

Comment apparaît cette phase verre de spin lorsque l'on abaisse la température ? S'agit-il d'une véritable transition au sens de la thermodynamique statistique, ou bien le système est-il "piégé" dans l'un de ses états ? Les expériences réalisées sur les verres de spin canoniques (type CuMn) et isolants (type EuSrS) semblent prouver (à ce jour) l'existence d'une transition qui se traduit principalement par une divergence de la susceptibilité non linéaire à la température (notée non plus T_g mais T_c désormais) où se produit le fameux cusp de susceptibilité.

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* On peut consulter à ce propos les revues de Rammal et Souletie [RS81] et de Toulouse [T81] dont sont largement inspirées ces quelques lignes.

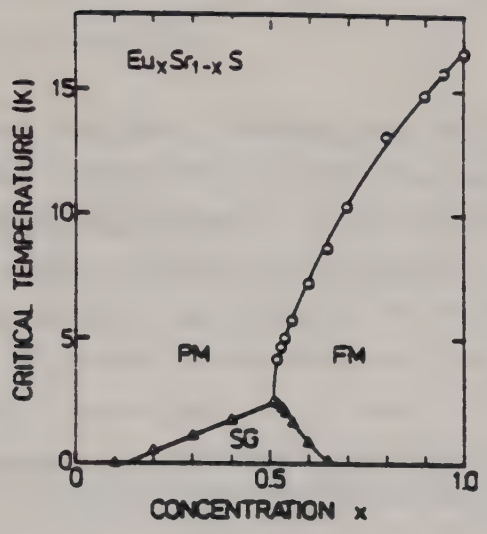

Figure A1 : Diagramme de phase de Eu Sr S (d'après [M80]).

PM : Phase para-magnétique

FM : Phase ferromagnétique

SG : Phase spin-glass

La compréhension théorique de cette transition repose actuellement sur la solution de Parisi d'un modèle dans lequel les spins sont tous couplés entre eux par des interactions aléatoires.

Le paramètre d'ordre de cette théorie est une fonction, associée à la brisure de symétrie entre les répliques du système, dont le sens physique reste obscur. Cette théorie rend qualitativement compte de nombreux résultats expérimentaux, et entre autres de la divergence de la susceptibilité non linéaire à T_c et du bris de la réponse linéaire au-dessous de T_c.

La transition verre de spin apparait dans ce cadre comme une transition extrêmement subtile, mais qui s'interprète à l'aide de la mécanique statistique à l'équilibre. Or l'analyse des simulations numériques fournit des conclusions inverses : la transition verre de spin ne serait qu'un ralentissement rapide de la dynamique, ralentissement subtil ici aussi, mais assez semblable au phénomène de transition vitreuse que présentent les verres conventionnels. Les expériences portant sur la dynamique des verres de spin montrent effectivement ce phénomène de ralentissement sans qu'une température critique n'apparaisse clairement.

Le problème de la transition n'est donc pas encore résolu, mais la richesse des phénomènes physiques découverts lors de son étude, tant expérimentale que théorique, est déjà remarquable.

Les verres conventionnels (voir l'encart "les verres")

Les verres sont des matériaux solides amorphes, dans lesquels les positions des atomes (ou entités chimiques) qui les constituent sont figées. Ce gel se produit dans une zone de température relativement étroite. A l'approche de cette zone, la viscosité du liquide croît plus vite qu'une loi d'Arrhénius, avec une dépendance en température de la forme* $\nu \approx \nu_o \exp(1/T-T_F)$. Au-dessous de la zone de gel, on observe des phénomènes de relaxation lente (volume, enthalpie ...), l'état vitreux étant un état intrinsèquement instable (et non métastable). A basse température, toutes les propriétés des verres peuvent s'interpréter à l'aide

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*Cette loi, dite loi de Fulcher-Vögel, souffre de quelques exceptions dont notamment la silice.

des systèmes à deux niveaux (la nature microscopique de ces excitations n'est d'ailleurs pas très bien élucidée).

Les verres sont des systèmes frustrés (frustration des liaisons chimiques) et désordonnés (plusieurs types d'atomes ; présence d'impuretés empêchant l'ordre cristallin d'apparaître), mais cet état des choses est plus la conséquence de l'impossibilité d'atteindre l'équilibre thermodynamique qu'une propriété de l'hamiltonien du système. Ce n'est seulement dans les verres de spin que les concepts de frustration et de désordre ont été quantifiés.

Ce bref aperçu montre que les systèmes frustrés désordonnés n'ont pas un comportement unique et que si la frustration et le désordre conjugués favorisent fortement l'existence d'une phase vitreuse, la façon dont cette phase apparaît n'est pas universelle.

II. UN ORDRE ORIENTATIONNEL DE TYPE VITREUX DANS L'HYDROGENE SOLIDE

L'hydrogène solide, le plus simple des solides moléculaires, présente un problème orientationnel qui incorpore naturellement frustration et désordre. Les molécules, fixées aux noeuds d'un réseau cristallin, sont de deux types : les molécules para (de moment orbital J=0) et les molécules ortho (J=1). Ces dernières sont réparties au hasard et se convertissent lentement en para. Au point de vue orientationnel, ce sont des quadrupoles électrostatiques couplés entre eux par les interactions quadrupolaires (les molécules para jouant le rôle d'un diluant inactif).

Il s'agit donc bien d'un système désordonné, frustré de plus, car aucune configuration de quadrupoles ne peut satisfaire les interactions en présence (cf. partie B). Son étude, lancée par les travaux précurseurs de N.S. Sullivan, a fait et continue de faire l'objet de nombreuses recherches. Un exposé des propriétés de ce système se trouve dans la thèse de M. Devoret [D82]. N. Sullivan et M. Devoret ont mis en évidence l'existence d'une nouvelle phase pour les concentrations intermédiaires de molécules ortho, phase qu'ils ont dénommée verre quadrupolaire - les degrés de liberté gelés étant ceux des moments quadrupolaires des molécules ortho -.

Cet ordre de type vitreux qui apparait progressivement, sans que l'on puisse détecter de transition au sens thermodynamique semble bien être cependant le résultat d'un phénomène coopératif.

Dans quelle mesure l'existence d'un verre dans un solide moléculaire frustré et désordonné était-elle un phénomène général ? Dans quelle mesure les effets quantiques importants observés dans l'hydrogène solide étaient il déterminants ?

C'est pour obtenir des éléments de réponse à ces questions que ce travail de thèse a été entrepris : les mélanges azote-argon sont en effet la contre-partie classique de l'hydrogène solide, les molécules d'azote étant l'analogue des molécules ortho, les atomes d'argon étant celui des molécules para. Au point de vue théorique, la quasi classicité de ce système le rend beaucoup plus simple que l'hydrogène solide. Au point de vue expérimental, la nature du réseau cristallin est mieux connue et il n'y a pas de problème de mise à l'équilibre thermique des échantillons.

III. PLAN DE THESE

Le présent travail a comporté tout d'abord une partie technique : la réalisation d'un appareillage permettant d'étudier la RMN de l'azote dans l'azote solide et les mélanges azote argon. Un bref exposé technique portant sur quelques aspects particuliers de cet appareillage est repoussé dans la partie G.

Les premières expériences réalisées ont montré que la RMN des molécules d'azote (et d'hydrogène) présente des particularités très intéressantes, susceptibles de fournir des informations importantes relatives au problème d'ordre orientationnal (présenté dans la partie B). Les nouvelles méthodes RMN que nous avons développées sont exposées dans la partie C, qui constitue le "coeur" de cette thèse.

Les résultats expérimentaux obtenus dans l'étude de l'azote pur et des mélanges azote-argon sont donnés respectivement dans les parties D et E.

Nous avons alors été conduit à effectuer la simulation numérique d'un ensemble de quadrupoles en interaction pour obtenir une meilleure compréhension des résultats expérimentaux. L'analyse de cette simulation fait l'objet de la partie F.

LES VERRES DE SPIN

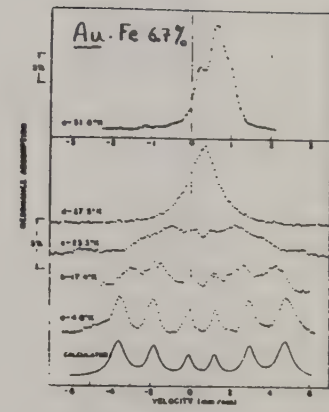
La phase verre de spin est caractérisée par la présence d'aimantations locales non nulles (1). L'apparition de cet ordre magnétique s'observe clairement sur un spectre Mössbauer (2) et sur un diagramme de μSR (3), sans qu'apparaisse cependant de singularité :

Les propriétés dynamiques changent de façon continue autour de la température de gel. Les mesures d'aimantation macroscopique (4) font apparaître par contre une température critique : la température en-dessous de laquelle l'aimantation d'un échantillon gelé sous champ (branche FC) diffère de celle d'un échantillon gelé en champ nul (branche ZFC) et mesurée dans un temps court (bris de la réponse linéaire). Aux temps longs, la branche ZFC rejoint le plateau FC avec une loi logarithmique. Le point anguleux de la branche ZFC s'arrondit lorsque le champ est augmenté, l'aimantation variant au-dessus de $T_g = T_c$ avec une loi de la forme :

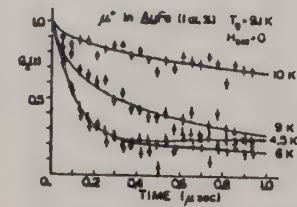
$$M = aH - \frac{bH^3}{(T-T_c)^\gamma} + \ldots$$

caractérisée par une divergence du terme non linéaire à la température critique. Alors qu'actuellement l'existence d'une transition en champ nul semble bien établie, la présence d'une ligne critique $H_c(T)$ prévue par la théorie est controversée.

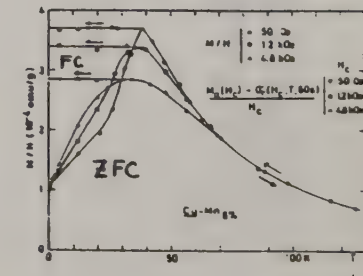
1. Une image de la phase verre de spin.



2. Spectres Mössbauer de AuFe (6.7% T_g=27.5K). Le spectre calculé correspond à des aimantations constantes des atomes de fer. On observe le passage progressif à un spectre rétréci par le mouvement sans singularité à la température de gel (d). Ces expériences fournissent des renseignements sur la dynamique des moments magnétiques autour de la fréquence hyperfine.



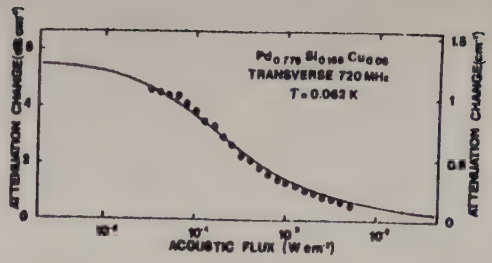
3. Fonction de relaxation en champ nul des muons dans AuFe (1%-T_g=0.1K). Les fits n'incorporent qu'un seul temps de corrélation (!) qui croît continuement lorsque l'on refroidit l'échantillon, avec une variation rapide autour de T_g. La μSR teste la dynamique des moments magnétiques à l'échelle du temps de vie des muons (2.2μs).

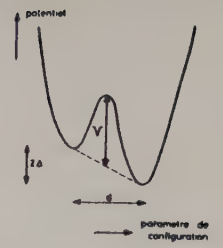


4. Courbes d'aimantation de CuMn (8%) dans différents champs. On observe l'arrondi du pic de la branche ZFC en champ et le plateau de la branche FC au-dessous de T_c.

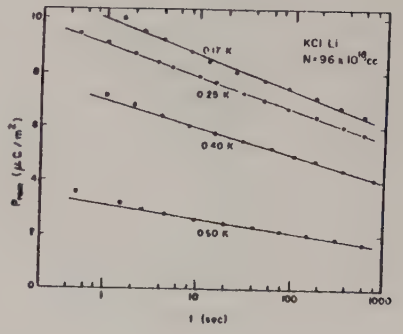
LES VERRES

Les verres sont des solides ne présentant pas d'ordre à longue distance. L'ensemble de leurs propriétés basse température s'interprète à l'aide d'un modèle d'excitations localisées indépendantes, décrites par des systèmes à deux niveaux dont les paramètres sont largement distribués. On rend ainsi compte notamment de la variation linéaire en température de la chaleur spécifique et de la saturation de l'absorption ultra sonore (1). L'apparition de la phase vitreuse lorsque l'on refroidit le liquide s'effectue dans une zone relativement étroite de température, ce qui permet de définir une température de gel. Elle se caractérise par une croissance extrêmement rapide des temps de relaxation (2). La phase vitreuse que l'on obtient ainsi dépend de la vitesse à laquelle la zone de transition a été franchie. C'est une phase instable dont l'évolution est extrêmement lente. Lorsque un paramètre externe est modifié au-dessous de la température de transition vitreuse, la quantité conjuguée rejoint sa valeur d'équilibre avec une loi logarithmique (3). La transition vitreuse relève de la mécanique statistique hors d'équilibre ; il n'en existe actuellement pas de modèle satisfaisant.

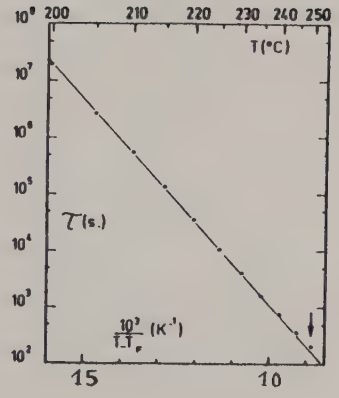




1. Saturation de l'absorption ultra sonore à fort niveau dans les verres : c'est la preuve directe du petit nombre de niveaux associés aux excitations. La ligne continue est obtenue dans le cadre du modèle des systèmes à deux niveaux.



2. Temps de relaxation du thermocourant en fonction de la température au-dessus de la température de gel dans un verre organique. On observe une loi de Vögel-Fulcher $\ell n\tau \propto 1/T-T_F$ avec $T_F = 410K$.



3. Polarisation rémanente à diverses températures d'un verre formé et refroidi sous champ. La relaxation logarithmique que l'on observe montre le caractère largement distribué des temps de relaxation des réarrangements atomiques.

PARTIE B :

LES MELANGES SOLIDES AZOTE-ARGON : UN SYSTEME DE QUADRUPOLES CLASSIQUES EN INTERACTION

I - L'ORDRE ORIENTATIONNEL DANS L'AZOTE SOLIDE

II - LE PROBLEME DE L'ORDRE ORIENTATIONNEL DANS LES MELANGES SOLIDES AZOTE-ARGON

III - COMPLEMENTS DE QUADRUPOLAROLOGIE CLASSIQUE

Présentation :

L'objet de cette partie est d'établir les données du problème de l'ordre orientationnel dans les mélanges solides azote-argon, et de préciser dans quelle mesure ce système est la réalisation d'un ensemble de quadrupoles classiques en interaction. Nous examinons tout d'abord le cas de l'azote pur pour lequel la validité de cette modélisation peut être mieux appréciée. Les paragraphes I et II font appel à des notions sur les quadrupoles qui sont développées dans le paragraphe III.

I. L'ORDRE ORIENTATIONNEL DANS L'AZOTE SOLIDE

Une revue très complète des propriétés physiques de l'azote a été donnée par T.A. Scott [S76], qui avait lui même beaucoup contribué à faire de l'azote le solide moléculaire le mieux connu. Ce paragraphe en est très largement inspiré.

1. LA MOLECULE D'AZOTE

Les noyaux

Il existe deux isotopes stables de l'azote, ^{14}N et ^{15}N, dont les propriétés sont résumées dans la table BI.

Comme nous le verrons dans la partie D, il est indispensable d'utiliser des échantillons enrichis en $^{15}N_2$ pour étudier l'ordre orientationnel dans les mélanges azote-argon par RMN. Nous signalerons donc chaque fois qu'elles sont significatives (et connues) les différences entre les propriétés de $^{14}N_2$ et celles de $^{15}N_2$.

La structure de la molécule

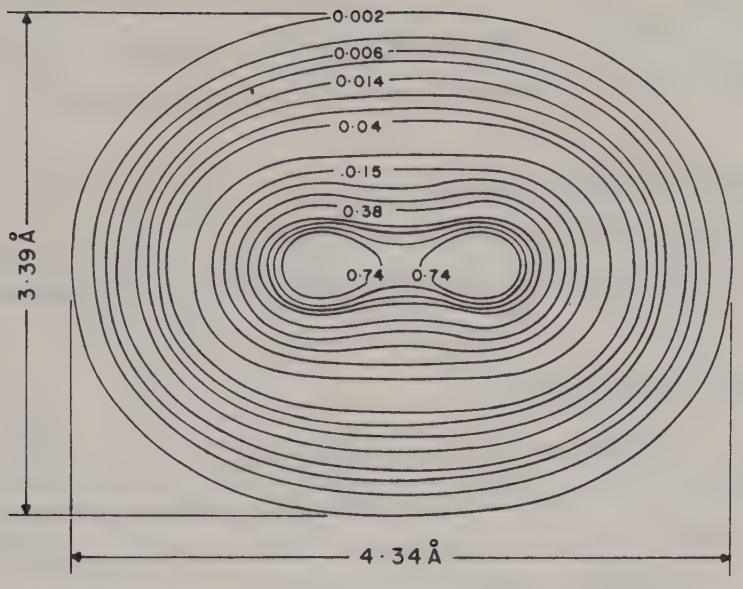
L'état fondamental de structure électronique $1\Sigma_g^+$ est assez distant en énergie des états excités électroniques et vibrationnels pour que l'on puisse considérer la molécule d'azote comme un objet rigide aux températures qui nous concernent ($T < 50K$). Une coupe de la carte de sa densité électronique est donnée sur la figure BI. La molécule d'azote apparaît comme un ellipsoïde de révolution relativement proche d'une sphère. Elle possède un moment quadrupolaire $Q_M = -1.4 \pm 0.1\ 10^{-26}$ esu.cm^2 qui est à l'origine d'un terme d'interaction quadrupolaire électrostatique (EQQ) dans le potentiel d'interaction de deux molécules. La distance internucléaire dans le solide est de 1.101 ± 0.003 Å [IS77].

2. LE POTENTIEL INTERMOLECULAIRE

Il n'existe pas de théorie complètement satisfaisante du potential d'interaction entre les molécules d'azote, et notamment de sa partie anisotrope. Il est certain que celle-ci est assez petite devant la partie isotrope pour que l'on puisse considérer le solide comme formé de molécules dont les centres de gravité sont fixés aux noeuds d'un réseau et couplées par des interactions orientationnelles. Le potentiel orientationnel n'est

isotope	abondance naturelle	spin nucléaire	facteur gyromagnétique (MHz/kG)	moment quadrupolaire eQ(barns)
^{14}N	99.63%	I = 1 (boson)	3.076	0.016
^{15}N	0.37%	I = 1/2 (fermion)	4.315	néant

TABLE B1 - LES ISOTOPES STABLES DE L'AZOTE



B1 - Coupe de la carte de densité électronique calculée de la molécule d'azote. Les contours sont donnés en unités de 6.749 e/Å^3. Le contour externe, qui contient plus de 95% de la charge totale, décrit bien la "forme" de la molécule.

pas connu avec précision et ne se limite pas aux interactions quadrupolaires électrostatiques (EQQ). Des formes plus complexes, incorporant un nombre croissant de paramètres, ont effectivement été développées.
Nous citerons pour mémoire les potentiels de Kohin (EQQ + interaction dispersive de London + interaction de recouvrement) et de Mandell (développement multipolaire contenant une douzaine de termes).

Il est cependant remarquable que la considération d'un potentiel quadrupolaire *effectif* suffise pour interpréter les propriétés *orientationnelles* de l'azote solide, du moins à pression nulle.

3. LES PHASES CRISTALLINES

L'azote cristallise en phase hexagonale (hc) dite phase β. L'azote solide présente une transition de phase du premier ordre à T=35.6K vers une phase cubique (cfc) dite phase α. Les données essentielles relatives à l'azote sont indiquées dans la table B2.

4. LA PHASE α

La phase α présente un ordre orientationnel identique à celui de l'hydrogène ortho pur. La structure, de symétrie Pa3, comporte quatre sous réseaux, les molécules de chaque sous réseau pointant en moyenne selon l'une des grandes diagonales du cube formant la maille élémentaire (figure B2).L'évolution du paramètre d'ordre p qui mesure cet alignement moyen (cf §.III) est indiquée sur la figure B3. On notera tout d'abord que p ne tend pas vers 1 lorsque T tend vers zéro : la valeur p=0.863 traduit l'existence d'un mouvement de point zéro orientationnel des molécules. Le calcul de cette légère délocalisation orientationnelle pour la structure Pa3 rend effectivement compte de cette valeur.

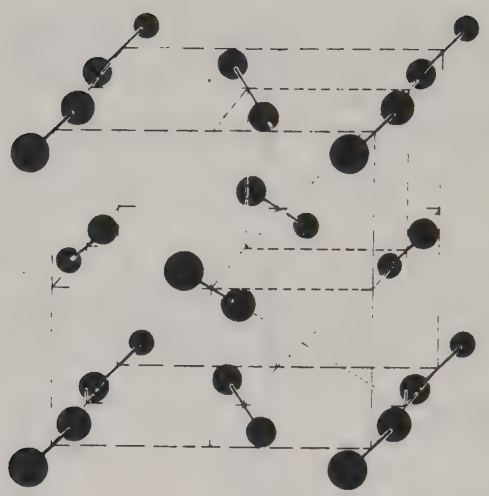
L'écart à la valeur p=1 prévue pour l'état fondamental d'un système de molécules classiques (masse infinie) mesure la "quanticité" résiduelle des molécules d'azote.

5. LA PHASE β

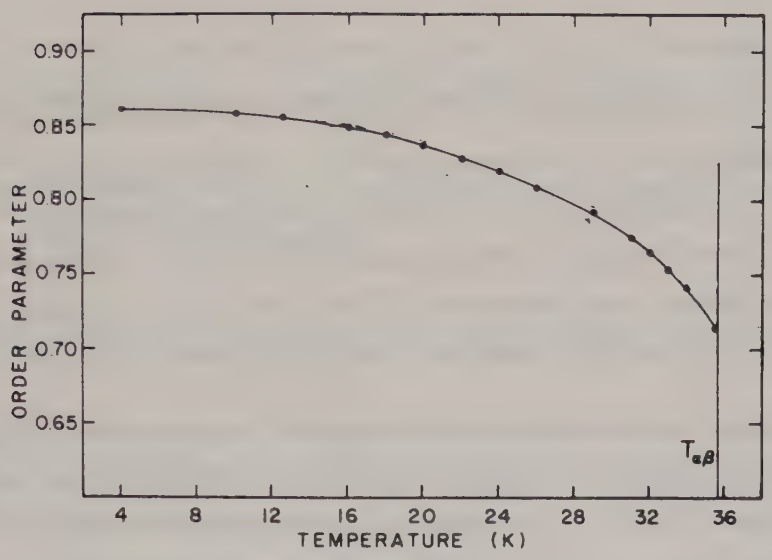
La phase β se caractérise essentiellement par l'absence d'ordre orientationnel, du moins si l'on se limite aux moments quadrupolaires.

	$^{14}N_2$	$^{15}N_2$
point triple (K)	63.14	63.19
chaleur latente de fusion (cal/mole)	172.26	172.21
température de transition α-β(K)	35.61	35.68
chaleur latente de transition (cal/mole)	55.62	56.61
paramètre cristallin a(Å) en phase α à 20K	5.660	5.645
température de Debye (K)	80.6	
Fréquence (GHz) du mode de libration E_g au centre de la zone de Brillouin	0.95	

TABLE B2 - PROPRIETES PHYSIQUES DE L'AZOTE



B2 - Structure Pa3 de l'azote solide. Les quatre molécules de base occupent quatre des huit sommets du petit cube intérieur. Le paramètre de la maille est de 5.660Å pour $^{14}N_2$ et 5.645Å pour $^{15}N_2$ à 20K.



B3 - Evolution du paramètre d'ordre $P=<\frac{3\cos^2\theta-1}{2}>$ de la structure Pa3 dans $^{14}N_2$ d'après l'étude du splitting dipolaire de la résonance quadrupolaire.

Les mouvements des molécules n'en sont pas pour autant décorrélés, comme le montre l'importance de la contribution orientationnelle à la chaleur spécifique. Une image fort parlante a été proposée pour décrire cette phase : celle d'un engrenage de roues dentées en prise les unes sur les autres et évitant d'être dent sur dent. Le problème de l'ordre orientationnel en phase β est abordé de façon plus détaillée dans la partie D.

6. SIMILITUDES ET DIFFERENCES AVEC UN SYSTEME DE QUADRUPOLES CLASSIQUES

Avant de détailler cette comparaison, il faut préciser que le problème de l'ordre orientationnel de quadrupoles classiques sur réseau cfc ou hc est loin d'être analysé théoriquement de façon satisfaisante. Il n'apparaitra pas alors très étonnant qu'une part importante des connaissances acquises sur ce système provienne de simulations numériques [M74].

Pour le réseau cfc, la structure d'énergie minimale est bien la structure Pa3. La frustration est également répartie entre toutes les liaisons : l'énergie de chaque lien n'est que la moitié environ (0.527) de l'énergie minimale possible pour un lien (configuration en T, cf.§.III). On prévoit théoriquement une transition vers une phase orientationnellement désordonnée, mais la prévision de l'ordre même de la transition (1er ordre) et plus encore de la température de transition est difficile pour ce système frustré : les corrélations sont importantes dans la phase désordonnée, et rendent ainsi délicate l'évaluation de l'énergie libre de cette phase. La simulation numérique est ici indispensable pour obtenir des résultats précis autorisant une comparaison significative avec l'azote solide. Mandell [M74] a effectué une telle simulation avec une centaine de quadrupoles sur les réseaux cfc et hc, en considérant des interactions quadrupolaires entre premiers et seconds voisins.

En attribuant à la constante de couplage Γ entre premiers voisins définie dans III la valeur $\Gamma \approx 9.7K$ (c'est-à-dire en ne considérant que les seules interactions EQQ) les résultats sont les suivants :

- La température de transition α-β obtenue est de $T_c = 4.05\Gamma$, soit $T_c \simeq 39.3K$ pour $\Gamma = 9.7K$. Mandell estime que les corrections quantiques produisent un abaissement de 10% environ, ce qui ramène alors la température critique très proche de la valeur expérimentale de 35.6K.

- La chaleur latente de transition est de L=2.9±0.3Γ cal/mole ce qui donne l'estimation L=56±5 cal/mole en excellent accord avec la valeur expérimentale L=56 cal/mole.

- Enfin la variation du paramètre d'ordre dans la phase ordonnée est en accord satisfaisant avec la dépendance observée expérimentalement, une fois pris en compte le mouvement de point zéro.

La transition orientationnelle de l'azote s'interprète donc correctement en considérant les seules interactions EQQ.

L'azote apparait de plus comme bien décrit par un système de quadrupoles *classiques* en interaction.

Cette analyse a cependant des limites, dont les principales dont :

i) Les fréquences libroniques calculées sont incorrectes et leur dépendence en pression prévue pour un simple hamiltonien quadrupolaire électrostatique n'est pas celle observée.

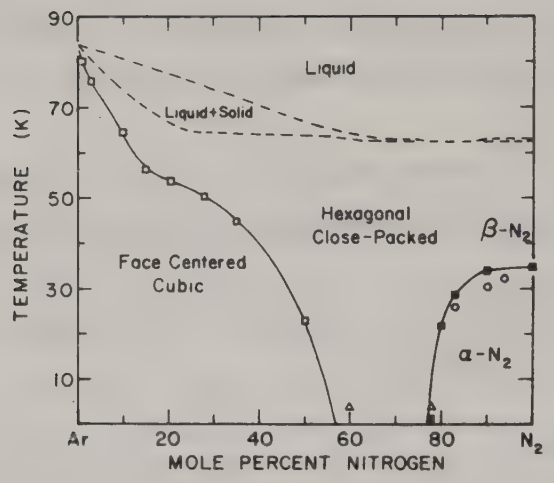
ii) Il existe une phase quadratique à haute pression dont l'interprétation nécessite l'introduction d'interactions de contact entre les couches électroniques externes de deux molécules.

Notre opinion est que la considération d'un hamiltonien quadrupolaire *effectif* constitue une bonne modélisation de l'azote solide à basse pression, du moins en ce qui concerne les propriétés statiques.

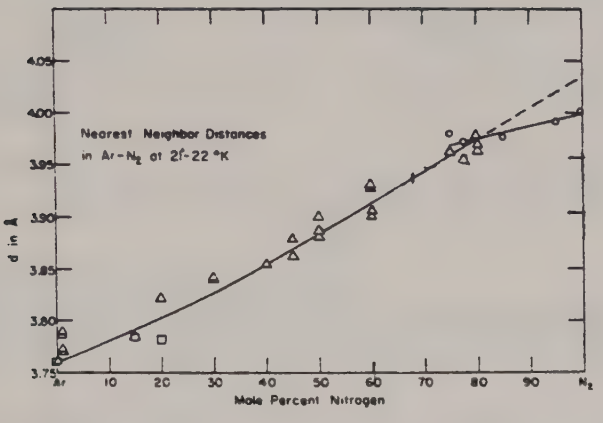
II. LE PROBLEME DE L'ORDRE ORIENTATIONNEL DANS LES MELANGES AZOTE-ARGON

1. DIAGRAMME DES PHASES CRISTALLINES

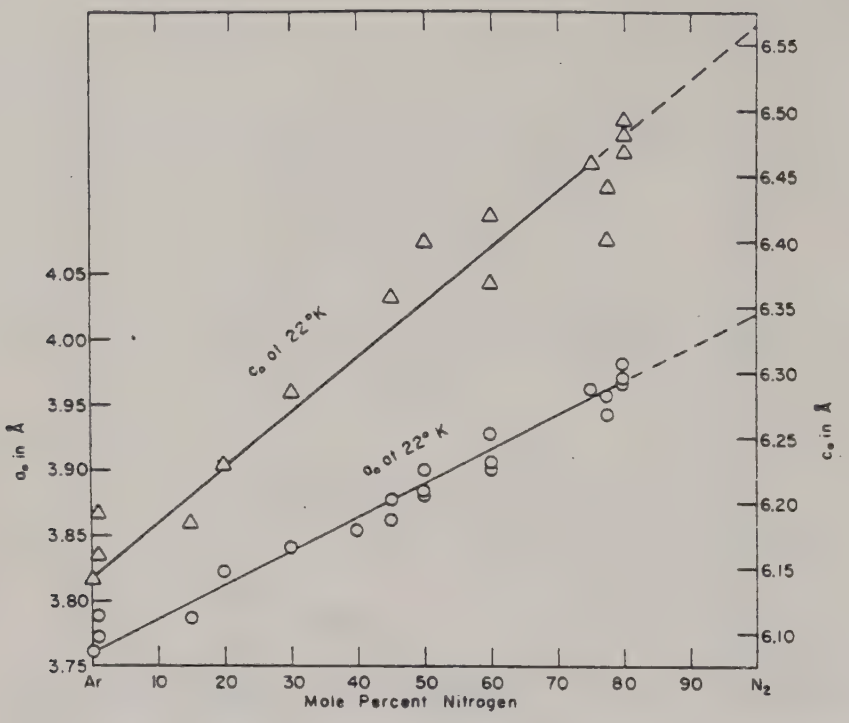
L'azote et l'argon sont miscibles en toutes proportions. Le diagramme des phases cristallines $N_{2(x)}-Ar_{(1-x)}$ obtenu par rayons X [BM65] est indiqué sur la figure B4.On notera la valeur élevée de la concentration critique X_c=0.77 d'existence de la phase α. La phase hexagonale est stable jusqu'à OK dans la zone de concentration 0.55<x<0.77. [PJG82]. Le domaine d'existence



B4 - Diagramme des phases cristallines des mélanges azote-argon. Les transitions entre phases solides sont soudaines et s'opèrent sans apparition de zones biphasiques dans le diagramme. La phase cubique riche en azote présente un ordre orientationnel à longue distance de type Pa3 [PJG82].



B5 - Distance minimale d'approche des centres des atomes et/ou des molécules dans les mélanges N_2-Ar à 22K.



B6 - Evolution des paramètres cristallins de la phase hexagonale en fonction de la concentration à T=22K.

de la phase cubique présente aux concentrations inférieures n'est pas très bien défini en raison d'un important hystérésis. La ligne de séparation indiquée sur le diagramme correspond à la limite supérieure observée de la zone d'instabilité de la phase hexagonale. La variation de la distance minimale d'approche entre premiers voisins avec la composition du mélange est indiquée sur la figure B5. L'évolution des paramètres c et a en phase hexagonale est donnée sur la figure B6.

Dans quelle mesure les molécules d'azote et les atomes d'argon sont-ils répartis au hasard sur les noeuds du réseau ? On peut estimer d'après les paramètres ε et r des potentiels Lennard-Jones des interactions azote-azote, azote-argon et argon-argon que le solide qui se forme à la solidification est homogène. Il le reste ensuite aux températures inférieures en raison de la lenteur de la diffusion dans le solide ([CE71] et partie D).

2. LE PROBLEME D'ORDRE ORIENTATIONNEL

Le réseau

Nous nous sommes intéressés dans ce travail au problème de l'ordre orientationnel en phase hexagonale, dans le domaine de concentration où celle-ci est stable jusqu'à T=0K.

Le potentiel orientationnel

Il est raisonnable de penser que la partie anisotrope du potentiel d'interaction entre les molécules d'azote est toujours correctement décrite par un potentiel quadrupolaire effectif. La constante de couplage Γ peut cependant voir sa valeur évoluer avec la concentration en raison de l'évolution de la taille de la maille cristalline (voir figures B4 et B5). Si l'on utilise pour évaluer cet effet les résultats obtenus dans l'étude de l'azote pur sous pression, on peut estimer que la constante de couplage de l'interaction quadrupolaire effective pour X=0.67 (soit à peu près au centre de la plage d'existence en concentration de la phase hexagonale à 0K) est environ 10% plus élevée que celle de l'azote pur, soit une modification relativement faible (en vue notamment des incertitudes diverses pesant sur la définition de Γ).

Le potentiel orientationnel comprend de plus des termes de champ cristallin (à un corps) résultant de la perturbation des cages de premiers voisins induite par le désordre. Ces termes n'ont été ni calculés ni mesurés. Leur ordre de grandeur est estimé tout au plus à quelques K, ce qui reste petit comparé à l'énergie minimale possible pour une seule liaison $-4\Gamma \approx 35K$.

Modélisation

Moyennant quelques réserves, le problème de l'ordre orientationnel dans les mélanges azote-argon aux concentrations intermédiaires $0.57<x<0.77$ est celui que présente un système de quadrupoles quasi classiques répartis aléatoirement aux noeuds d'un réseau hexagonal compact.

La validité de cette modélisation est discutée au vu des résultats expérimentaux dans la partie E. On peut par ailleurs noter les points suivants :

i) Le diagramme de phase des mélanges solides azote-argon ressemble à celui des mélanges ortho-para d'hydrogène solide pour lequel la modélisation par un hamiltonien quadrupolaire est excellente. Tous deux contiennent une phase hc et une phase cfc stable au-dessus d'une concentration critique (0.55 dans l'hydrogène solide).

ii) La valeur élevée de cette concentration critique se comprend bien dans le cadre de cette modélisation : La structure Pa3 très frustrée est facilement destabilisée par le désordre. On peut effectivement montrer [D80] que dans le cadre d'un modèle simplifié des interactions entre molécules la structure Pa3 n'est stable qu'au-dessus d'une concentration critique très supérieure au seuil de percolation du réseau.

3. UN SYSTEME DU TYPE VERRE DE SPIN ?

Nous développons ici le parallèle entre les systèmes dilués de quadrupoles en interaction et les systèmes magnétiques dilués donnant lieu à des phases verre de spin.

Un SDQ est un système frustré désordonné, et les analogies avec un système du type $Eu_xSr_{1-x}S$ (cf partie A) sont nombreuses comme le montre la table B3.

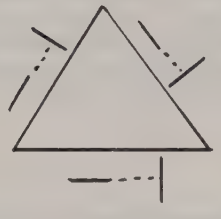
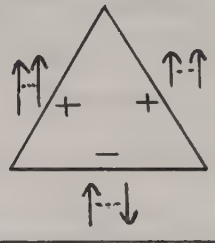
les degrés de liberté	orientation d'une tige	orientation d'un spin
les interactions	- courte portée - quadrupolaires déterminées par l'orientation de la liaison considérée	- courte portée - super échange déterminées par la position dans le réseau des spins considérés
symétries globales	néant	SO3
l'origine de la frustration (les symboles représentent un état d'énergie minimale pour la liaison)		
propriétés en l'absence de désordre	sur réseau cfc : - structure ordonnée Pa3 - transition du 1er ordre	- structure ordonnée ferromagnétique - transition du 2ème ordre
type de désordre	substitutionnel (diluant inactif)	substitutionnel (diluant inactif)

TABLE B3 - SIMILITUDES ET DIFFERENCES ENTRE UN SDQ ET LE SYSTEME ($Eu_xSr_{1-x}S$).

La différence la plus significative apparait dans l'absence d'une symétrie globale d'un système de quadrupoles : rien n'interdit aux quadrupoles d'un SDQ d'avoir des orientations préférentielles et une quadrupolarisation (définition simplifiée : mesure du degré d'alignement d'un quadrupole avec certaines directions ; cf §.III) non nulle à haute température sans qu'aucune symétrie du système n'ait été brisée. Cet effet apparait explicitement dans un développement haute température au deuxième ordre en 1/T pour un quadrupole sur un réseau cfc ou hcp dont la cage de premiers voisins est incomplète (cf.§.III).

Un système de spins en champ nul possède par contre au moins la symétrie d'inversion $\vec{S} \to -\vec{S}$, ce qui assure qu'en l'absence du bris de cette symétrie la polarisation d'équilibre thermique d'un spin ne peut qu'être nulle. Corrélativement, l'observation de polarisations locales non nulles *prouve* que le système n'explore plus qu'une partie de l'espace de phase. Le problème de l'ordre orientationnel dans un SDQ est donc différent du problème de l'ordre magnétique dans un verre de spin isolant dans le sens où le désordre local induit des quadrupolarisations non nulles à toute température. Les conséquences de cet effet sont abordées dans la partie F.

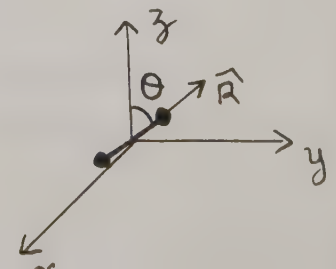
Le fait d'étudier des quadrupoles n'est pas aussi sans conséquences sur le plan expérimental : il est exclu de mesurer (du moins directement) l'analogue de l'aimantation dans un système de spins sous champ. Il s'agirait en effet de mesurer la réponse du système à un gradient de champ électrique - et ce gradient devrait atteindre des valeurs comparables à celles qui règnent dans le solide pour entraîner effectivement les molécules ! -

III. COMPLEMENTS DE QUADRUPOLAROLOGIE "CLASSIQUE"

1. DESCRIPTION DE L'ETAT ORIENTATIONNEL D'UNE MOLECULE

Considérons le problème d'une molécule symétrique (telle que N_2) dans un gradient de champ électrique axial. Le potentiel orientationnel est simplement :

$$V = -\varepsilon P_2(\theta) = -\varepsilon \left(\frac{3\cos^2\theta - 1}{2} \right)$$



où θ est l'angle entre un vecteur unitaire $\hat{R}$ de coordonnées x_α lié à l'axe de la molécule et l'axe Oz.

L'effet du gradient de champ électrique est d'aligner la molécule le long de l'axe Oz si ε est positif ou bien de la coucher dans le plan xOy si ε est négatif. La quantité p qui mesure cet alignement (positif ou négatif) est simplement la valeur moyenne $\langle P_2(\theta)\rangle$. Dans l'approximation classique, cette moyenne statistique est donné par :

$$p = \langle P_2(\theta)\rangle = \frac{\int_0^1 e^{\frac{\varepsilon}{kT}\left(\frac{3u^2-1}{2}\right)} \left(\frac{3u^2-1}{2}\right) du}{\int_0^1 e^{\frac{\varepsilon}{kT}\left(\frac{3u^2-1}{2}\right)} du}$$

La variation avec la température de p est donnée dans la figure B7.

Pour décrire l'état orientationnel d'une molécule placée dans un gradient de champ électrique quelconque ou bien en interaction avec d'autres molécules il faut considérer toutes les composantes du tenseur quadrupolaire $\overline{\overline{Q}}$ ($\equiv$ quadrupolarisation) ainsi défini :

composantes sphériques

$$Q_m = \sqrt{\frac{4\pi}{5}} \langle Y_{2m}(\hat{R})\rangle$$

composantes cartésiennes

$$Q_{\alpha\beta} = \langle x_\alpha x_\beta\rangle - \frac{\delta_{\alpha\beta}}{3}$$

soit :

$$Q_0 = \frac{3\langle z^2\rangle - 1}{2}$$

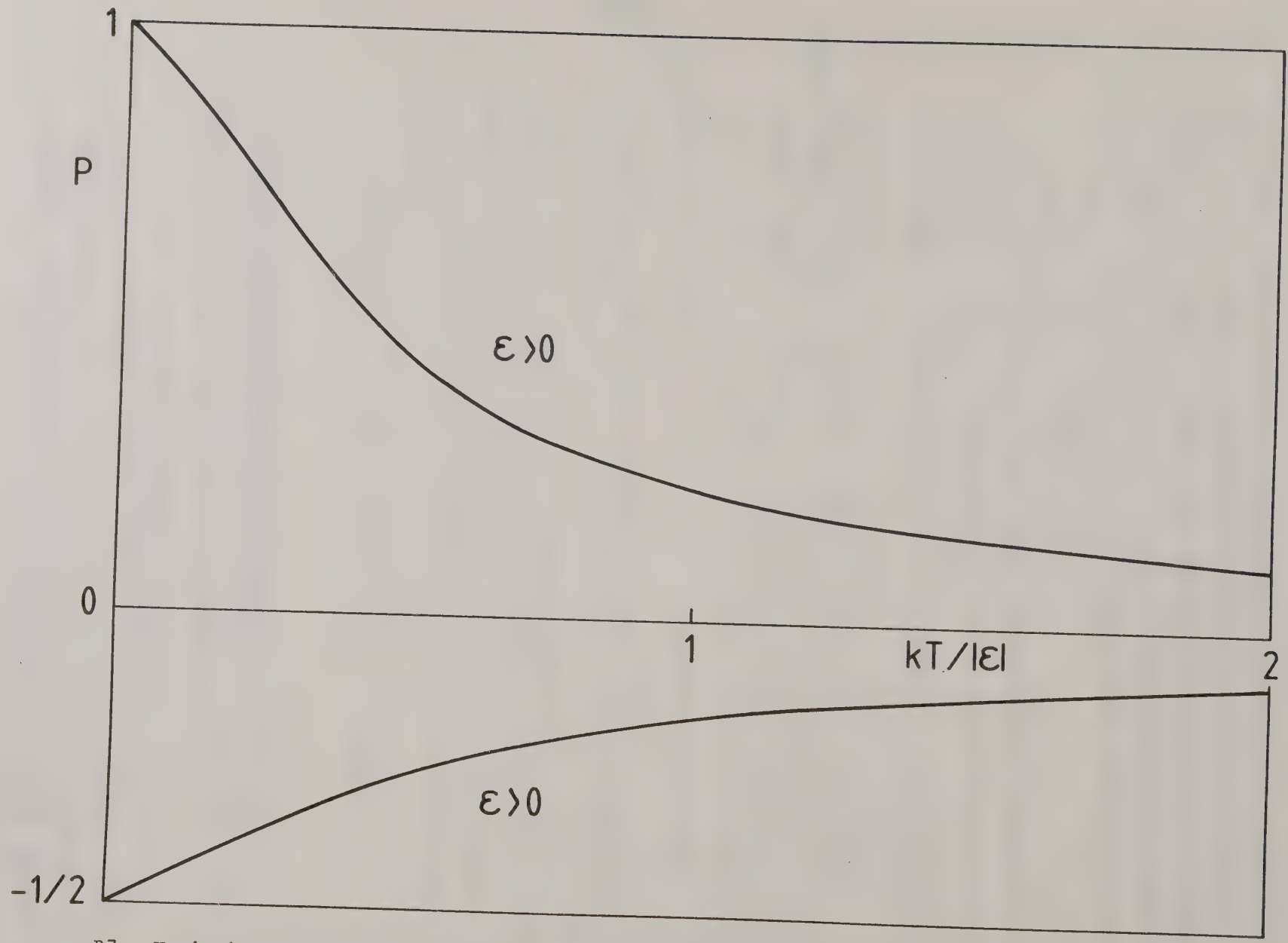
$$Q_{\pm 1} = \mp\sqrt{\frac{3}{2}}\left(\langle xz\rangle \pm i\langle yz\rangle\right)$$

$$Q_{\pm 2} = \sqrt{\frac{3}{2}}\left(\frac{\langle x^2\rangle - \langle y^2\rangle \pm 2i\langle xy\rangle}{2}\right)$$

Dans un changement d'axes, les Q_m se transforment par les matrices de rotation de rang 2 $D^{(2)}_{m'm}$:

$$Q'_{m'} = \sum_m D^{(2)}_{m'm} Q_m \ .$$

Ces nouvelles composantes ont une expression particulièrement simple dans le repère qui diagonalise la forme quadratique f(x,y,z) associée à $\overline{\overline{Q}}$:



B7 - Variation thermique de l'alignement d'une molécule de symétrie de type tige placée dans un gradient de champ électrique. Le calcul effectué dans l'approximation classique est valide lorsque la température est grande devant la constante rotationnelle de la molécule.

les seules composantes non nulles sont alors Q'_o et $Q'_{\pm 2}$; Une représentation de $\bar{\bar{Q}}$ est fournie par l'ellipsoïde d'équation f=0, soit dans ce nouveau repère :

$$\frac{x'^2}{\langle x'^2\rangle} + \frac{y'^2}{\langle y'^2\rangle} + \frac{\langle z'^2\rangle}{\langle z'^2\rangle} = 1$$

Pour une tige fixe, cet ellipsoïde n'est autre que la tige elle même. Pour une tige pointant au hasard dans toutes les directions, cet ellipsoïde est une sphère de rayon $1/\sqrt{3}$. L'écart à la sphère de rayon $1/\sqrt{3}$ est mesuré par les deux paramètres :

$$\sigma = Q'_o = \frac{3\langle z'^2\rangle - 1}{2}$$

$$\eta = \frac{1}{\sqrt{2}}\left(Q'_2 + Q'_{-2}\right) = \frac{\sqrt{3}}{2}\left(\langle x'^2\rangle - \langle y'^2\rangle\right)$$

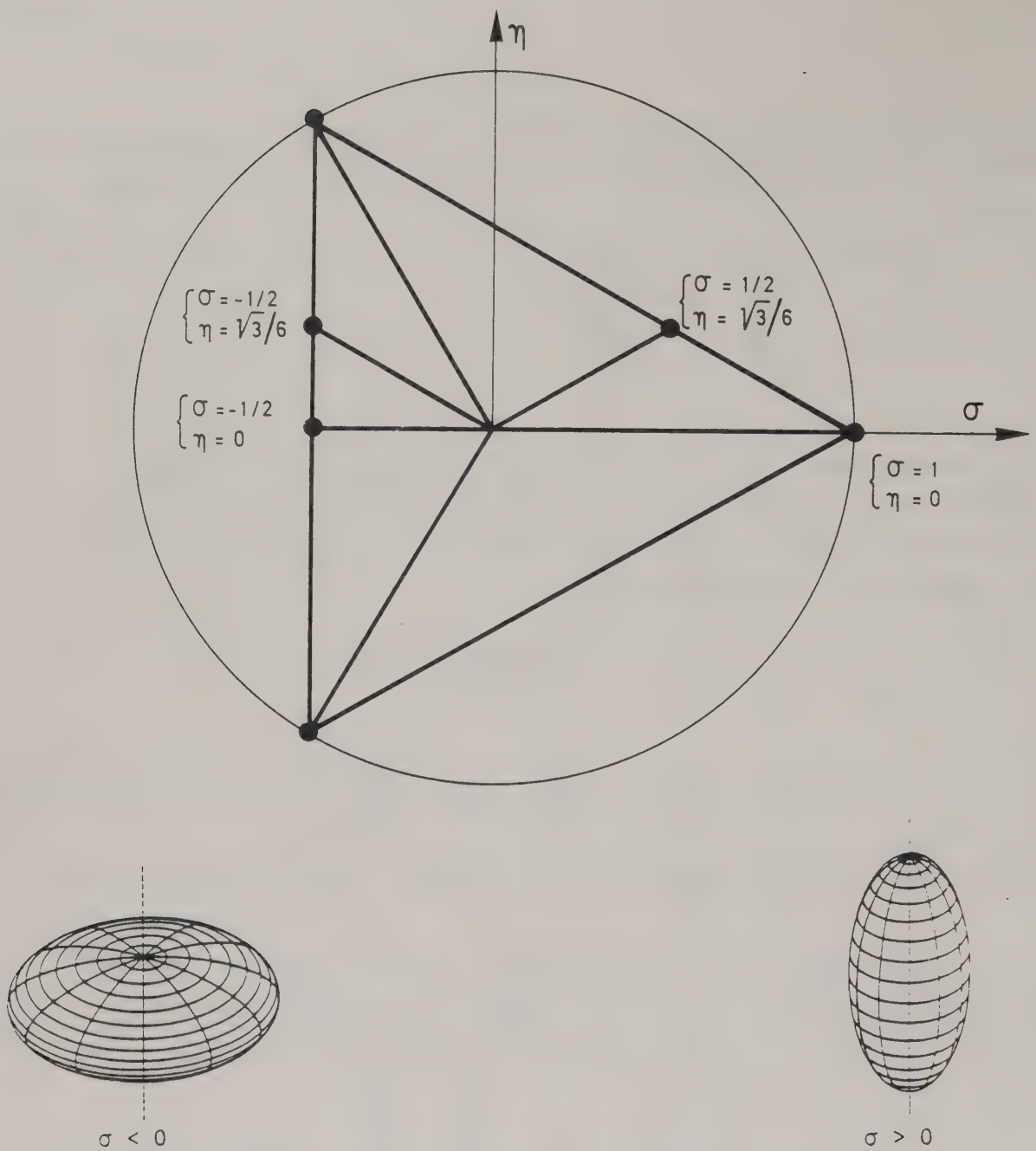
Le domaine des valeurs possibles pour σ et n est indiqué sur la figure B8.

La quadrupolarisation d'une molécule se décrit donc par la donnée d'un trièdre et du couple (σ,n). Elle représente le premier terme du développement en moments multipolaires de la densité de présence de l'axe de la molécule.

Pour des molécules comme H_2, D_2 ou N_2, le spectre RMN est directement lié à la distribution des quadrupolarisations dans l'échantillon. Plus précisément, le spectre RMN fournit la fonction de distribution de la composante Q_o si le champ magnétique est aligné sur l'axe Oz. (cf partie C).

2. L'INTERACTION QUADRUPOLAIRE

Le terme quadrupolaire dans l'énergie d'interaction de deux molécules 1 et 2 est proportionnel à la quantité scalaire que l'on peut bâtir à partir des harmoniques sphériques de rang 2 : $Y_{2m}(\hat{R}_1)$, $Y_{2n}(\hat{R}_2)$ et des harmoniques sphériques de rang 4 : $Y_{4m'}(\hat{R}_{12})$.



B8 - Lieu des valeurs permises pour les paramètres de quadrupolarisation σ et η . Ces frontières résultent de la positivité de $\langle x^2 \rangle$, $\langle y^2 \rangle$ et $\langle z^2 \rangle$. Lorsque l'on impose que η soit positif et de plus le plus petit possible, les couples (σ,η) sont limités à la zone grisée. Les ellipsoides décrivant l'état de quadrupolarisation de la molécule sont alors proches d'un cigare pour $\sigma > 0$ ou d'un disque pour $\sigma < 0$.

Il s'écrit* :

$$E_{QQ} = \Gamma \frac{32\pi}{45}\sqrt{70\pi} \sum_{m\,n} C^{224}_{mn}\, Y^{*}_{4m+n}(\hat{R}_{12})\, Y_{2m}(\hat{R}_1)\, Y_{2n}(\hat{R}_2) \qquad (1)$$

Une expression plus simple s'obtient dans un repère d'axe Oz parallèle à $\vec{R}_{12}$ en considérant des combinaisons réelles des harmoniques sphériques :

$$E_{QQ} = \frac{4}{3}\Gamma\, {}^{t}\tilde{q}_1 \begin{pmatrix} 6 & & \\ & -4 & 0 \\ & -4 & 1 \\ 0 & & 1 \end{pmatrix} \tilde{q}_2$$

avec la définition

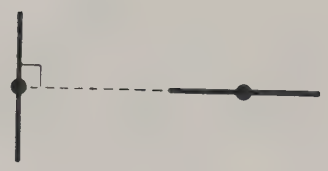
$$\tilde{q}(\hat{R}) = \begin{pmatrix} \frac{3z^2-1}{2} \\ \sqrt{3}\,yz \\ \sqrt{3}\,xz \\ \sqrt{3}\,xy \\ \frac{\sqrt{3}}{2}(x^2-y^2) \end{pmatrix}$$

Les énergies de quelques configurations typiques sont indiquées sur la figure (B9).

La configuration d'énergie minimale (-4Γ) est la configuration dite en T. Des quadrupoles aux noeuds d'un réseau tridimensionnel constituent un système frustré car il est impossible d'assurer cette configuration en T pour toutes les paires de quadrupoles voisins.

---

* Dans le cas d'une interaction quadrupolaire électrostatique, la constante de couplage Γ est reliée au moment quadrupolaire Q des quadrupoles par la relation $\Gamma = 6e^2Q^2/25R^5$.



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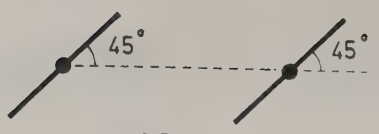
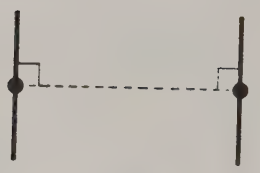


$-\frac{13}{4}$

$\frac{19}{4}$



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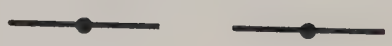

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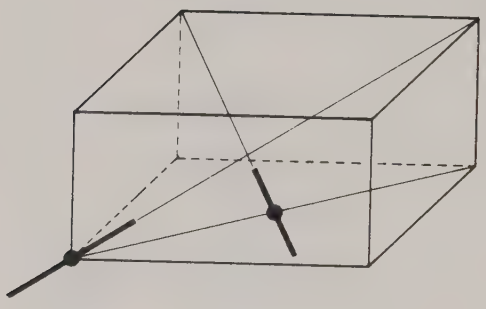


$-\frac{19}{9}$

B9 - Energies de quelques configurations simples d'une paire de quadrupoles (unité Γ). L'énergie minimale -4Γ est obtenue pour les configurations en T (noter la dégénérescence) ; l'énergie maximale 8Γ est obtenue pour la configuration en ligne (unique).

3. LE DEVELOPPEMENT HAUTE TEMPERATURE

Nous calculons ici le premier terme du développement haute température en 1/T des quadrupolarisations dans un système de quadrupoles classiques en interaction. Ce calcul est très similaire à celui effectué par Harris [H70] dans le cas de quadrupoles "quantiques" de moment orbital J=1.

Considérons l'hamiltonien quadrupolaire suivant :

$$H = \sum h_{ij}(\Omega_i, \Omega_j)$$

où h_{ij} est l'hamiltonien (1) d'interaction des quadrupoles i et j repérés par les angles Ω_i et Ω_j. La composante Q_{im} de la quadrupolarisation du quadrupole i est donnée par :

$$Q_{im} = \sqrt{\frac{4\pi}{5}} \frac{\underset{\cdots j \cdots}{\mathrm{tr}}\, Y_{i2m}(\Omega_i)\, e^{-\beta H}}{\underset{\cdots j \cdots}{\mathrm{tr}}\, e^{-\beta H}}$$

où le symbole de trace signifie une intégration sur les variables angulaires. Le premier terme à considérer dans le développement en puissances de $\beta = 1/T$ est :

$$Q_{im} = \frac{\beta^2}{2}\sqrt{\frac{4\pi}{5}} \sum_{\substack{j \text{ voisin} \\ \text{de } i}} \underset{(i,j)}{\mathrm{tr}}\, Y_{2m}(\Omega_i)\, h_{ij}^2(\Omega_i, \Omega_j) + \cdots$$

Les contributions dues aux différents voisins d'un site s'ajoutent donc au second ordre.

Pour une paire de quadrupoles isolée, la quadrupolarisation de chacun ne peut être qu'axiale, l'axe de révolution de l'ellipsoïde de quadrupolarisation étant parallèle à la droite joignant les deux quadrupoles.

Il suffit donc de calculer la composante Q_o dans un repère dont l'axe Oz est parallèle à cette droite. L'opération de trace nécessite la sommation des termes suivants :

$$\sum_{\substack{m\,n\\ m'n'}} \left(C^{224}_{mn}\, C^{224}_{m'n'}\, Y^{*}_{4\,m+n}(\Omega_{12})\, Y^{*}_{4\,m+n'}(\Omega_{12}) \int \frac{d\Omega_1}{4\pi}\, Y_{20}(\Omega_1)\, Y_{2m}(\Omega_1)\, Y_{2m'}(\Omega_1) \right.$$

$$\left. \times \int \frac{d\Omega_2}{4\pi}\, Y_{2n}(\Omega_2)\, Y_{2n'}(\Omega_2) \right)$$

qui obéissent aux règles de sélection :

$$m + n = 0$$

$$m' + n' = 0$$

$$m + m' = 0$$

$$n + n' = 0 \quad .$$

Après calcul des intégrales et sommation, on obtient au 2ème ordre :

$$Q_0 = \frac{32}{63} (\beta\Gamma)^2 = \sigma \qquad (\eta = 0)$$

L'ellipsoïde de quadrupolarisation est donc du type cigare. Soulignons le côté paradoxal de ce résultat : bien que les quadrupoles évitent la configuration d'énergie maximale dans laquelle ils sont tous deux alignés le long de l'axe qui les joint, l'effet moyen des corrélations orientationnelles qui se développent entre eux est cependant de les aligner le long de cet axe.

Utilisant les propriétés de rotation des harmoniques sphériques, on obtient plus généralement (au deuxième ordre en β) : pour un quadrupole interagissant avec des voisins :

$$Q_{i\,m} = \sqrt{\frac{4\pi}{5}}\, \frac{32}{63} (\beta\Gamma)^2 \sum_{\substack{j \text{ voisin}\\ \text{de } i}} Y_{2m}(\Omega_{ij})$$

Cette expression est nulle pour les réseaux cfc et hc lorsque tous les sites sont occupés par des quadrupoles.

Si l'on supprime un quadrupole, les voisins du "trou" adoptent des quadrupolarisations qui sont au second ordre les mêmes que s'ils interagissaient seulement avec un "antiquadrupole" : ils s'orientent de façon à

éviter la direction du trou avec une quadrupolarisation : (cf fig.B10)

$$\sigma = -\frac{32}{63}(\beta\Gamma)^2$$

$$\eta = 0$$

Lorsque les quadrupoles sont répartis aléatoirement (en concentration X) sur les noeuds d'un réseau, les quadrupolarisations calculées au second ordre sont distribuées et ne sont plus axiales. On peut cependant calculer la moyenne d'ensemble du module de quadrupolarisation :

$$q = \overline{\sigma_i^2 + \eta_i^2}$$

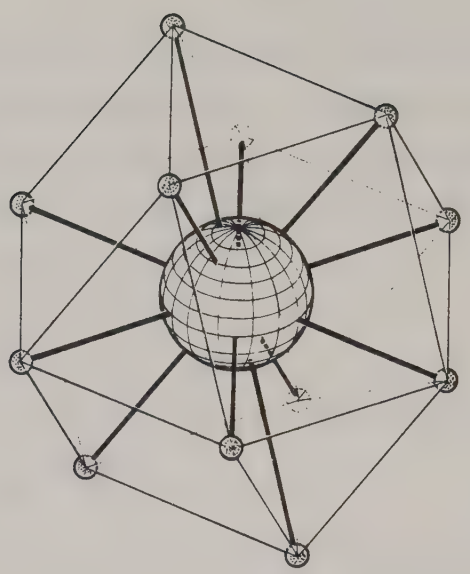
On obtient au second ordre pour les réseaux cfc et hc :

$$q = 12X(1-X)\left(\frac{32}{63}\right)^2 (\beta\Gamma)^4$$

expression qui met en évidence la symétrie entre les concentrations X et (1-X) qui existe à haute température.

La présence de quadrupolarisations non nulles à haute température dans un système dilué de quadrupoles en interaction traduit le fait que le désordre brise la symétrie rotationnelle à toute température. Ce phénomène est lié à la non invariance par rotation globale des quadrupoles de l'hamiltonien quadrupolaire.

cage
complète



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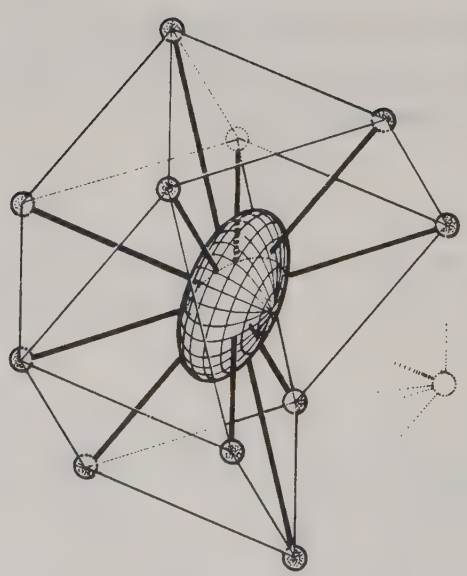

B10 - Modification de l'ellipsoïde de quadrupolarisation induite à haute température par la suppression d'un quadrupole de la cage des premiers voisins (réseau cfc).

PARTIE C :

LES METHODES RMN D'ETUDE DE L'ORDRE ORIENTATIONNEL

INTRODUCTION

I - RMN ET ORDRE ORIENTATIONNEL

II - L'ANALYSE DES FORMES DE RAIE RMN

III - LES METHODES D'ECHOS ET LA DETECTION DES MOUVEMENTS DE ROTATION

IV - RELAXATION LONGITUDINALE ET FLUCTUATIONS ORIENTATIONNELLES

INTRODUCTION

L'objet de cette partie est de présenter ce qu'offre la RMN dans l'étude de l'ordre orientationnel de molécules du type azote ou hydrogène. Mais quels sont tout d'abord les autres moyens d'investigation de l'ordre orientationnel que l'on peut mettre en oeuvre ?

Il faut tout d'abord citer les mesures thermodynamiques telles que les mesures de chaleur spécifique. Elles sont significatives lorsque l'on a une assez bonne connaissance des contributions des autres degrés de liberté (tels que translationnels) pour pouvoir isoler ce qui est dû à l'ordre orientationnel.

Les méthodes qui sont sensibles aux orientations des molécules sont de deux types. Elles utilisent soit :

a) l'anisotropie de la distribution de la charge électronique dans une molécule,
soit
b) la position relative des noyaux d'une molécule.

Les méthodes du type a) sont principalement la diffusion X et la diffusion Raman. La diffraction X est délicate à mettre en oeuvre car les molécules d'hydrogène et d'azote ont une distribution de charge quasi sphérique. C'est néanmoins ainsi que la structure Pa3 de l'azote solide a été identifiée.

La diffusion Raman est par contre une méthode très sensible qui donne accès aux énergies des excitations orientationnelles. Silvera [S80] a notamment étudié ainsi le diagramme de phase de l'hydrogène sous pression. Le spectre d'absorption d'énergie par les degrés de liberté orientationnels dans l'infrarouge fournit aussi le même type de renseignements [BCDM79].

Les méthodes du type b comprennent l'ensemble des techniques neutroniques et la RMN.

Les neutrons donnent accès à différents types d'informations selon la technique employée. La présence d'une structure orientationnelle

ordonnée à longue distance apparait sur le spectre de diffraction. Le spectre de diffusion inélastique fournit par ailleurs des informations sur la dynamique des molécules aux temps courts (la limite étant donnée par l'inverse de la résolution en fréquence des neutrons observés). L'utilisation de ces méthodes dans l'étude des mélanges azote-argon a fait l'objet d'un travail récent par Press et al.[PJG82] qui est commenté dans la partie E.

I. RMN ET ORDRE ORIENTATIONNEL

La RMN permet d'étudier l'ordre orientationnel car il existe un hamiltonien de couplage entre les degrés de liberté nucléaires et les degrés de liberté orientationnels. Au point de vue RMN, H_2 et $^{15}N_2$ solides sont des paires de spin 1/2 faiblement couplées entre elles par des interactions dipolaires. La molécule $^{15}N_2$, tout comme la molécule d'hydrogène , existe sous deux espèces ortho (I=1) et para(I=0). On n'observe par RMN que les molécules ortho. Le couplage dipolaire entre les deux noyaux d'une molécule ortho prend la forme suivante :

$$H_{D\,intra} = -\frac{\hbar^2\gamma^2}{R^3}\sqrt{\frac{24\pi}{5}}\sum_{m=-2}^{2} I^2_{\bar{m}}\, Y_{2m}(\Omega)$$

où γ est le facteur gyromagnétique, R la distance entre les noyaux d'une molécule d'orientation repérée par Ω et les I^2_m les opérateurs tensoriels irréductibles de rang 2 du spin I=1 (cf. table C1). Pour les molécules d'azote, l'hamiltonien intramoléculaire contient de plus un terme de déplacement chimique anisotrope traduisant l'anisotropie de la perturbation de la fonction d'onde électronique induite par un champ magnétique. Ce terme prend la forme suivante(*) lorsque le champ est appliqué selon l'axe oz :

$$H_{\chi\,intra} = \sum_{m=-1}^{1} \hbar\omega_\chi\, C^{211}_{m\bar{m}}\, I^1_{\bar{m}}\, Y^2_m(\Omega)$$

(*) Cette forme s'obtient ainsi : à partir du champ appliqué $\underset{\sim}{H}$ et de l'orientation de la molécule on construit un champ $\underset{\sim}{h}$; l'hamiltonien est alors proportionnel à $\underset{\sim}{h}.\underset{\sim}{I}$.

$K = 1$

$$\begin{cases} I^1_0 = \dfrac{I_z}{\sqrt{2}} \\ I^1_{\pm 1} = \mp \dfrac{1}{2}\left(I_x \pm I_y\right) = \mp \dfrac{1}{2} I_\pm \end{cases}$$

$K = 2$

$$\begin{cases} I^2_0 = \dfrac{1}{\sqrt{6}}\left(3 I_z^2 - 2\right) \\ I^2_{\pm 1} = \mp \dfrac{1}{2}\left(I_\pm I_z + I_z I_\pm\right) \\ I^2_{\pm 2} = I_\pm^2 \end{cases}$$

TABLE C1 - OPERATEURS TENSORIELS IRREDUCTIVLES I^K_Q
DU SPIN I=1

où ω_χ est une fréquence proportionnelle au champ et C^{---}_{--} un coefficient de Clebsh Gordan.

En champ élevé, lorsque les interactions nucléaires (1) et (2) sont petites devant l'hamiltonien Zeeman , il faut séparer dans 1 et 2 la partie séculaire a) m=0 des termes non séculaires b) m≠0.

a) La partie séculaire induit un déplacement des niveaux nucléaires de la molécule d'une quantité proportionnelle à $Y_{20}(\Omega)$. L'analyse de la forme de raie RMN et de l'amortissement des échos fournit donc des informations sur l'évolution des fonctions $Y_{20}(\Omega_i(t))$. Plus précisément, la forme de raie est déterminée par les valeurs moyennes de ces fonctions (valeurs moyennes temporelles, mesurées sur une échelle de temps de l'ordre de l'inverse de la largeur de raie rigide). Une étude quantitative de la forme de raie ne peut être tentée que dans le cas où l'évolution des $Y_{20}(\Omega_i(t))$ autour de leurs valeurs moyennes s'effectue à une fréquence élevée devant les fréquences caractéristiques des interactions nucléaires intramoléculaires : elle fournit alors la distribution des quadrupolarisations des molécules. Nous avons effectué cette analyse dans le cas de l'hydrogène solide (paragraphe II) et des mélanges azote-argon (cf partie E).

L'analyse de l'amortissement de divers échos permet de suivre les orientations des molécules sur une échelle de temps beaucoup plus longue que celle qui intervient dans la forme de raie. Il devient alors possible de déceler une évolution lente de l'état de quadrupolarisation des molécules. Nous montrons en particulier que les échos stimulés obtenus après une séquence de trois impulsions permettent de détecter des mouvements de rotation des molécules se produisant à une fréquence extrêmement basse. Un tel élargissement de la gamme des échelles de temps accessibles à la RMN est notamment précieux lorsque l'on étudie des phases de type vitreux pour lesquelles de tels mouvements lents sont possibles. La mise en oeuvre des méthodesd'échos est présentée dans le paragraphe III.

b) La partie non séculaire des interactions nucléaires induit des transitions entre les niveaux nucléaires d'une molécule. Le couplage avec le mouvement de rotation des molécules est un mécanisme de relaxation de l'aimantation longitudinale. Le taux de relaxation T_1^{-1} de ce mécanisme fait intervenir la densité spectrale des fonctions $Y_{2m}(\Omega(t))$ aux

fréquences $|m|\omega_{Larmor}$. L'analyse du problème de la relaxation longitudinale pour les molécules dans des états orientationnels bien définis est développée dans le paragraphe IV.

Une synthèse des méthodes développées dans cette partie est présentée dans le paragraphe V pour le cas d'école de molécules classiques agitées d'un mouvement brownien de rotation de temps caractéristique variable.

II - L'ANALYSE DES FORMES DE RAIE RMN

ARTICLE :

ON THE DISTRIBUTION OF LOCAL QUADRUPOLARISATIONS IN THE ORIENTATIONAL GLASS H_2

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On the distribution of local quadrupolarisations in the orientational glass H_2

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Abstract. We present a detailed study of the NMR spectra of solid H_2 in the intermediate ortho-concentration regime ($0.20 \leqslant X \leqslant 0.55$). This system displays a glassy orientational behaviour resulting from quadrupolar interactions and site disorder. We obtain the distribution function for the local quadrupolarisations which describe the extent to which the molecular orientations are frozen. We observe broad distributions that evolve only smoothly with temperature. This behaviour suggests a continuous growth of quadrupolarisations on cooling without any abrupt transition.

1. Introduction

The simplest molecular solid H_2 constitutes, as far as orientational properties are concerned (Silvera 1980), a system that incorporates both frustration and disorder. Let us recall that in solid H_2 the two molecular species—ortho-molecules ($J = 1$, concentration X) and para-molecules ($J = 0$)—are randomly distributed on the sites of a lattice. The ortho-molecules interact via short-range orientationally dependent interactions—essentially quadrupolar—whereas the para-molecules simply play the role of an inactive diluent. The system is frustrated in the sense that the pairs of quadrupoles cannot all reach their minimum-energy state (obtained for an isolated pair) in any many-body ground state. One expects from the combined presence of frustration and disorder that this system will display a glassy behaviour, i.e. frozen-in molecular orientations without any long-range order. Indeed, a consensus has been reached among experimentalists that solid H_2 (and D_2) presents this kind of ordering at low temperatures and intermediate concentrations ($0.20 \leqslant X \leqslant 0.55$) (Sullivan *et al* 1978, Washburn *et al* 1980, Cochran *et al* 1980, Candela *et al* 1981, Haase and Saleh 1981).

However, a detailed description of the manner by which the glassy ordering is established in this system has not been given. Whereas previous studies based the discussion of the existence of a possible transition to a glassy phase on the analysis of a *few* features of the NMR lineshapes, we present here an interpretation supported by the maximum amount of information that can be extracted from the NMR spectra: the *distribution* of local quadrupolarisations. The q adrupolarisation is the parameter that describes the extent to which the orientation of a molecule is localised. It is the analogue for rod-like molecules of the polarisation for spins. The key result of this detailed analysis

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of previous experimental work (Sullivan *et al* 1978) is the temperature dependence of the quadrupolarisation distribution‡.

2. The NMR spectrum and the quadrupolarisation distribution

The full density matrix that describes the orientational state of the system is

$$\rho = e^{-\beta\mathcal{H}}/\mathrm{tr}\, e^{-\beta\mathcal{H}} \tag{1}$$

with the following quadrupolar Hamiltonian:

$$\mathcal{H} = \sum_{\langle ij\rangle, mm'} \Gamma_{ij}^{mm'} \Theta_{im} \Theta_{jm'}. \tag{2}$$

The Θ_m are the normalised irreducible tensorial operators of rank 2 in the manifold $J = 1$ (see table 1); the indices i and j label the ortho-molecules. The operators Θ_m play

Table 1. Normalised irreducible tensorial operators of rank 2 in the manifold $J = 1$. Their scalar products are given by $\mathrm{tr}(\Theta_m \Theta_n^\dagger) = \delta_{mn}$.

$\Theta_0 = 6^{-1/2}(3J_Z^2 - 2)$
$\Theta_{\pm 1} = \mp\frac{1}{2}(J_Z J_\pm + J_\pm J_Z)$
$\Theta_{\pm 2} = \frac{1}{2}J_\pm^2$

for quantum rotators (here the ortho-molecules, $J = 1$) the role of the operators S_m for spins. In contrast with the Heisenberg Hamiltonian

$$H = \sum_{(i,j)} J_{ij} S_{im} S_{jm}^\dagger$$

the quadrupolar Hamiltonian incorporates the anisotropic matrix $\Gamma_{ij}^{mm'}$:

$$\Gamma_{ij}^{mm'} = (\tfrac{4}{5}\pi \times 70)^{1/2} \Gamma_{ij} C_{mm'}^{224} Y_{m+m'}^{4*}(\Omega_{ij}) \tag{3}$$

where $\Gamma_{ij} = 6e^2Q^2/25R^5 \simeq 0.8$ K for i and j nearest neighbours, $Y_m^l(\Omega)$ is a spherical harmonic, $C_{m_1M_2}^{l_1l_2l_3}$ is a Clebsch–Gordan coefficient, Q is the quadrupole moment of the H_2 molecules, R is the intermolecular distance and $\Omega_{ij} = (\hat{R}_{ij}, \hat{Z})$. The Z axis belongs to the laboratory frame which is used to define the Θ_m.

Each ortho-molecule i carries a total nuclear spin $I = 1$ whose energy levels are given by the intramolecular dipolar Hamiltonian:

$$\hbar^{-1}\mathcal{H}_D = D \sum_m \Theta_{im} T_{im}^\dagger \qquad D/2\pi = 174 \text{ kHz} \tag{4}$$

where the T_m are the irreducible tensors of rank 2 for the nuclear spin $I = 1$ of an ortho-molecule.

In order to interpret the NMR lineshapes, we introduce the following hypotheses.

(i) The fluctuations of the molecular orientations are very fast compared with the relevant frequency for NMR lineshapes measurements, i.e. the intramolecular dipolar frequency D. In this case, NMR lineshapes depend only on single-particle thermodynamic

‡ As this work was being completed we learned from Professor Horst Meyer that his group at Duke University has carried out the same type of analyses of the CW spectra and has obtained similar results for the quadrupolarisation distribution (Washburn *et al* 1982a).

averages, and therefore can be used only to determine the local reduced density matrices σ_i. These matrices have the following form for $J = 1$ molecules:

$$\sigma_i = \tfrac{1}{3}\mathbf{1} + \sum_{m=-1}^{1} \langle J_{im}^{+} \rangle J_{im} + \sum_{m=-2}^{2} \langle \Theta_{im}^{+} \rangle \Theta_{im} \tag{5}$$

where the brackets denote the thermodynamic average

$$\langle A_i \rangle = \mathrm{tr}(\rho A_i). \tag{6}$$

This hypothesis is supported by the results of various NMR spin-echoes experiments (Estève and Sullivan 1982, Yu *et al* 1982) which clearly show that one never observes an intermediate motional narrowing regime in samples of intermediate ortho-concentration.

(ii) The average orbital moments $\langle J_{im} \rangle$ are all zero. This hypothesis of quenching of the orbital moment has always been assumed in previous analyses of solid H_2 NMR spectra (Reif and Purcell 1953). In fact, it can be derived from the invariance of the quadrupolar Hamiltonian under any site-parity transformation.

(iii) In the local frame $(\hat{\xi}, \hat{\eta}, \hat{\zeta})_i$ of each molecule i, such that the matrix representating σ_i is diagonal (such a frame always exists when hypothesis 2 is valid), the only non-zero quadrupolar moment is

$$\langle \theta_{i0} \rangle = \langle (3J_{i\zeta_i}^2 - 2)/6^{1/2} \rangle. \tag{7}$$

This is equivalent to assuming an axial symmetry around ζ_i for the quadrupolar component of σ_i. This is a simplifying hypothesis which does not crucially affect the results and which will be discussed later.

Under the assumptions (1) and (2), the two Zeeman transitions of an ortho-molecule i are slightly shifted from the Larmor frequency by the amounts

$$\omega_i = -(D6^{1/2}/2)\langle \Theta_{i0} \rangle \qquad \omega_i' = +(D6^{1/2}/2)\langle \Theta_{i0} \rangle. \tag{8}$$

These formulae arise from the secular part (that is the $m = 0$ component when H_0 is applied along the $\hat{Z}$ axis) of the intramolecular dipolar Hamiltonian (4).

Taking into account hypothesis (3), one obtains by using the transformation properties of irreducible tensors of rank 2 under rotations:

$$\omega_i = -(D6^{1/2}/2)\left[(3\cos^2\alpha_i - 1)/2\right]\langle \theta_{i0} \rangle \tag{9}$$

where α_i is the angle between $\hat{\zeta}_i$ and $\hat{Z}$. Introducing the local quadrupolarisations x_i:

$$x_i = -(6^{1/2}/2)\langle \theta_{i0} \rangle = \langle (2 - 3J_{i\zeta_i}^2)/2 \rangle \tag{10}$$

one obtains

$$\omega_i = Dx_i(3\cos^2\alpha_i - 1)/2. \tag{11}$$

For a powdered sample, the distribution function $\mathcal{P}(x)$ of x_i is uncorrelated with the distribution of the α_i, and one can write the NMR spectrum $S(\omega)$ as

$$S(\omega) = \left(\int_{-1/2}^{1} \mathrm{d}x\, \mathcal{P}(x)\, \Pi(x, \omega) \right) * g(\omega) \tag{12}$$

where $\Pi(x, \omega)$ denotes the well known Pake doublet of frequency span $2D|x|$ (see figure

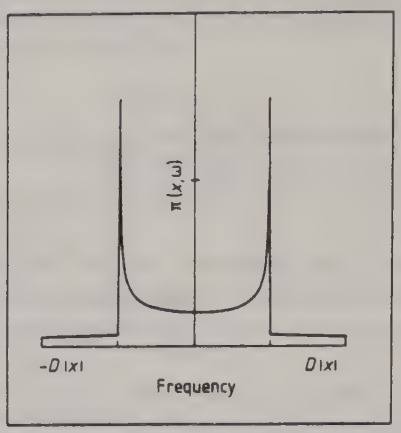


Figure 1. The Pake doublet spectrum which is the theoretical lineshape of an assembly of randomly oriented molecules with a given axial quadrupolarisation $x = \langle (2 - 3J_z^2)/2 \rangle$. $D/2\pi = 174$ kHz is the intramolecular dipolar constant.

1) and $g(\omega)$ denotes an appropriate convolution function which takes into account the intermolecular dipolar broadening:

$$\Pi(x, \omega) = (\Delta(Dx, \omega) + \Delta(-Dx, \omega)) \tag{13}$$

$$\Delta(y, \omega) = 3^{-1/2}(2\omega y + y^2)^{-1/2} \qquad \text{when } (\omega - y)(\omega + y/2) < 0.$$

$$= 0 \qquad \text{otherwise.}$$

The function $g(\omega)$ is given by the Fourier transform of the observed spin-echo damping factor (Estève and Sullivan 1982). For the sake of simplicity, we have approximated this Fourier transform by the product of a Lorentzian and a Gaussian of appropriate widths:

$$g(\omega) \propto \frac{\exp(-\omega^2/3.1\Delta^2)}{[1 + (\omega/\Delta)^2]} \qquad \text{with } \Delta/2\pi = 7.2\,(X^{1/2}) \text{ kHz.} \tag{14}$$

3. Extraction of the quadrupolarisation distribution from NMR spectra

An ideal analysis of the spectra would be to compute $\mathcal{P}(x)$ once $S(\omega)$ is given by an 'inversion' of formula (12).

A first limitation arises from the invariance of $\Pi(x, \omega)$ under the transformation $x \to -x$. This invariance implies that $S(\omega)$ can be rewritten as

$$\begin{aligned} S(\omega) &= \left(\int_0^1 dx\, (\mathcal{P}(x) + \mathcal{P}(-x))\, \Pi(x, \omega) \right) * g(\omega) \\ &= \left(\int_0^1 dx\, P(x)\, \Pi(x, \omega) \right) * g(\omega) \end{aligned} \tag{15}$$

where $P(x)$ is simply the distribution function for $|x|$. It is only this distribution function that can be unambiguously extracted from the spectra. It is clear that if (15) has a solution $P(x)$, it is unique and positive if the above hypotheses leading to (12) are true.

To our knowledge, no stable inversion procedure exists for this problem. We have

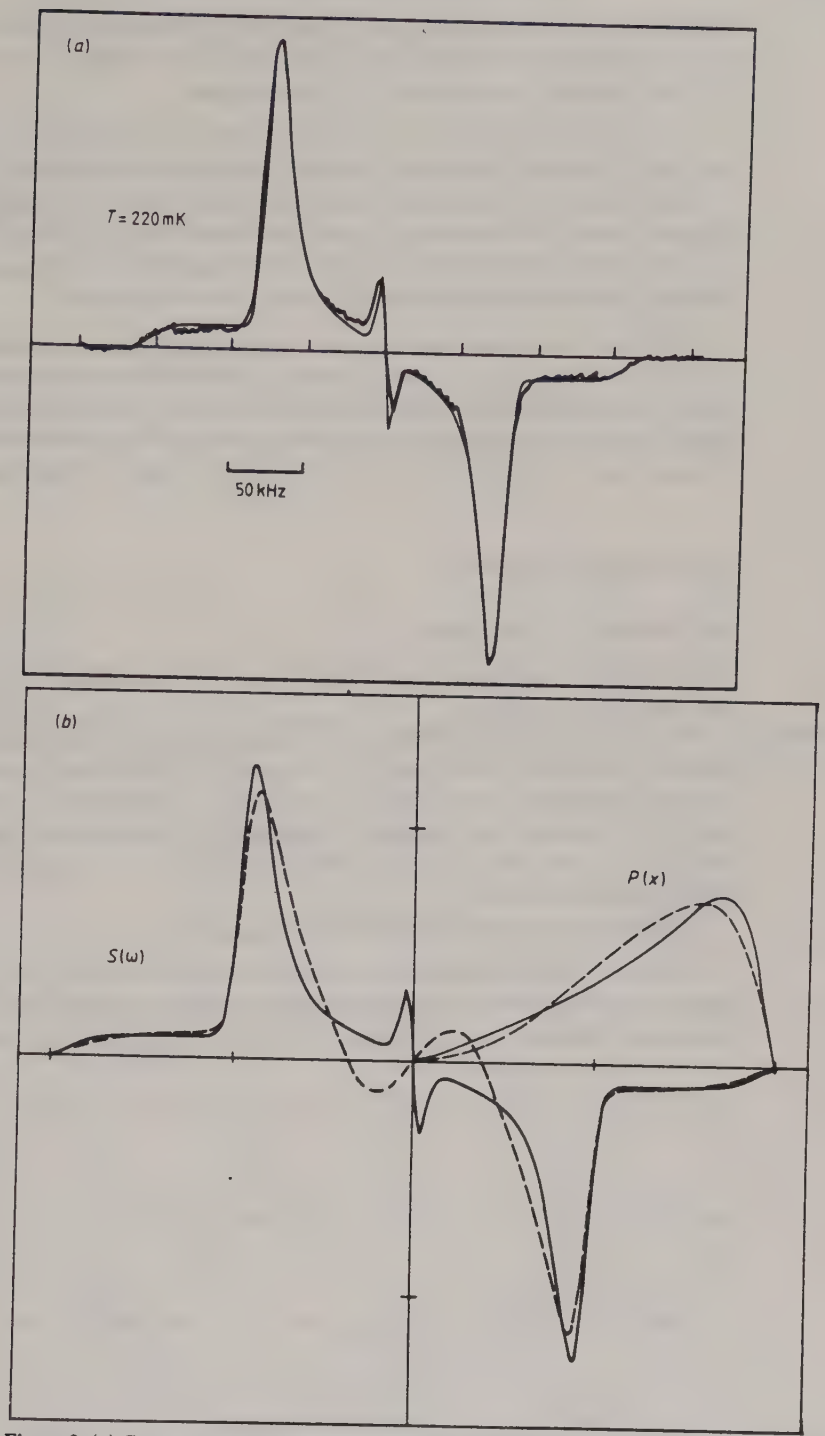


Figure 2. (*a*) Comparison between an experimental lineshape derivative and the synthesised shape that gives the best fit. (*b*) Comparison between two synthesised lineshape derivatives resulting from two slightly different distributions $P(x)$. (The full curves correspond to the case of figure 2(*a*).) This comparison gives an idea of the precision achieved in the determination of $P(x)$.

thus been led to synthesise spectra with trial functions $P(x)$ until a 'reasonable' fit with the experimental data (lineshape derivatives) was achieved. More precisely, a desk-top HP 9825 computer was used in the following way:

(*a*) given an analytical trial function for $P(x)$, 50 equidistant samples were generated and used to define a piecewise-constant function on the interval [0, 1];

(*b*) this function was then used as input to an analytical calculation of an intermediate spectrum which was thereafter convoluted numerically for 200 points;

(*c*) the finite-difference derivative of the spectrum was computed. Hence, a direct comparison with raw experimental data could be performed.

$P(x)$ was chosen among simple analytical expressions for a first gross fit. This fit was then refined by taking for $P(x)$ a cubic spline function interpolating nine adjustable points. It was found that $S(\omega)$ is very sensitive to the detailed shape of $P(x)$; we have thus reasonable confidence in the determination of $P(x)$ at least as far as its overall shape is concerned. One can get an idea of the precision that has been achieved from figure 2.

4. Results and discussion

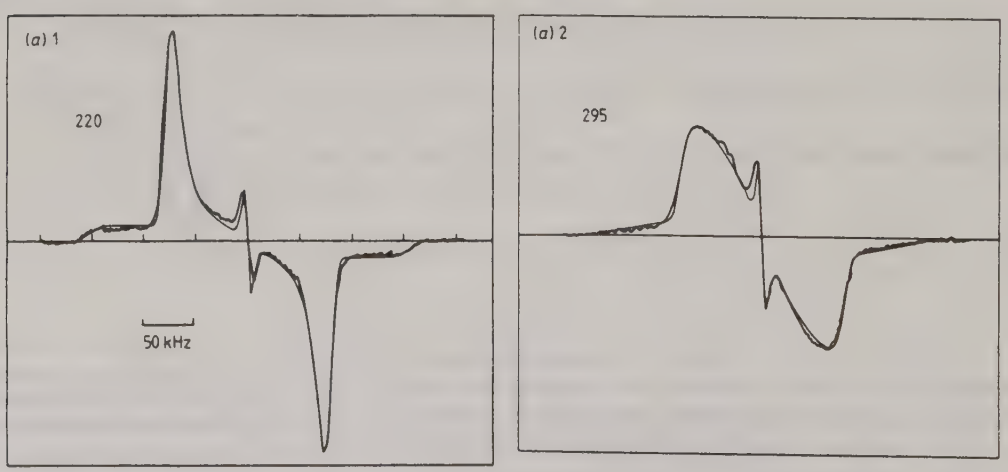
4.1. Analysis of NMR spectra

Two series of NMR spectra corresponding to ortho-concentrations $X = 0.53$ and 0.37 were analysed.

The best fits for both samples are shown in figure 3. The quadrupolarisation distributions $P(x)$ for the corresponding samples at various temperatures are given in figure 4. At temperatures higher than those shown in these figures, $P(x)$ changes in a trivial way by just contracting along the x direction. At lower temperatures $P(x)$ evolves only very slowly from the $P(x)$ corresponding to the lowest temperature of the series of spectra shown in figure 3.

The results suggest the following observations.

(i) $P(x)$ is a broad, apparently featureless, distribution as already reported by Sullivan *et al* (1978). However, their proposed rectangular shape was not correct since their 'calculated' lineshape would actually require a triangular form $P(x) = 2x$ for $0 < x < 1$.



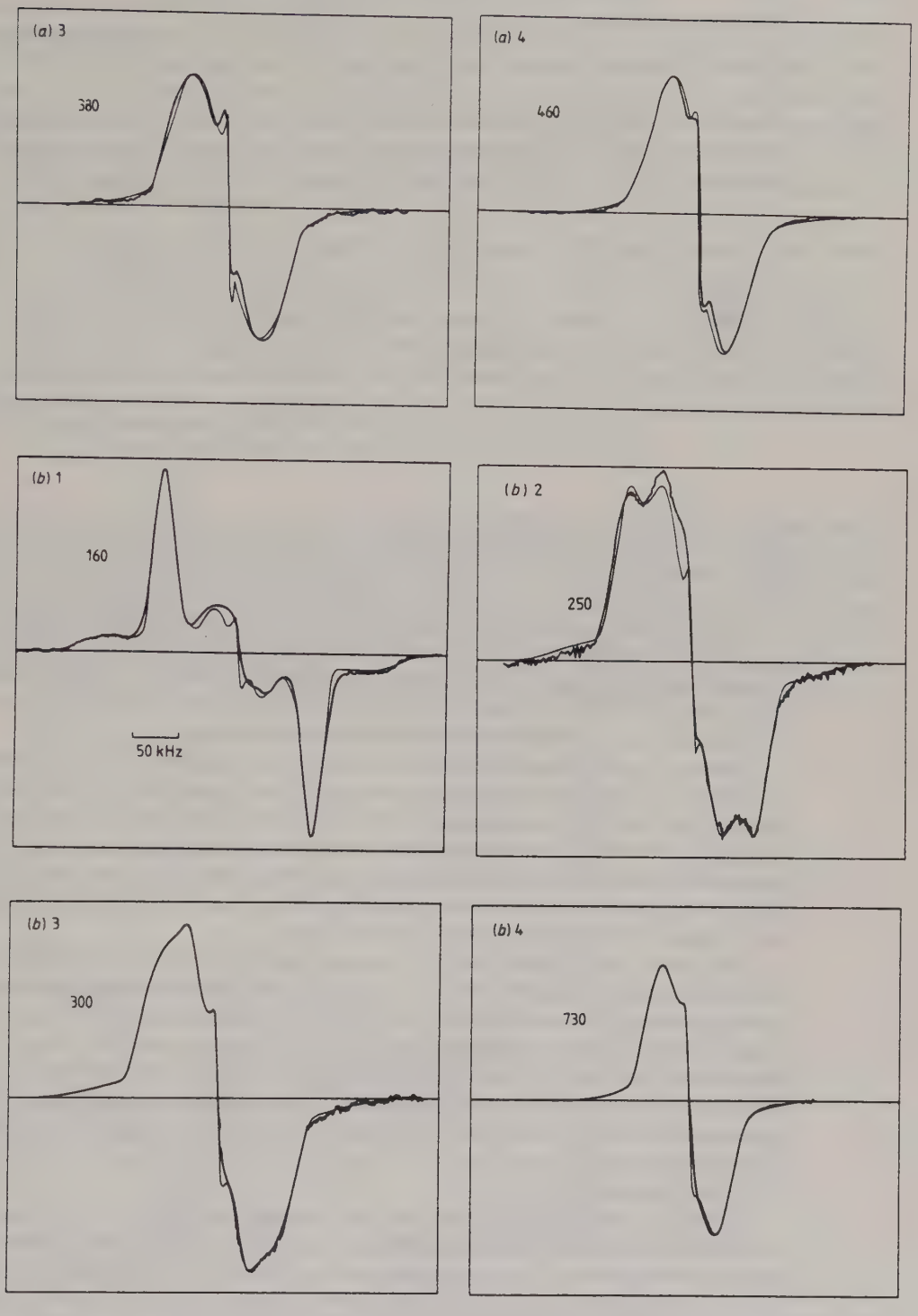


Figure 3. Lineshape derivatives at various temperatures (given in mK in figures) together with their best fits for samples with ortho-hydrogen concentrations of X = (*a*) 0.53, (*b*) 0.37. (Only half of the experimental spectra are shown in figures 3(*b*) parts 3–4.)

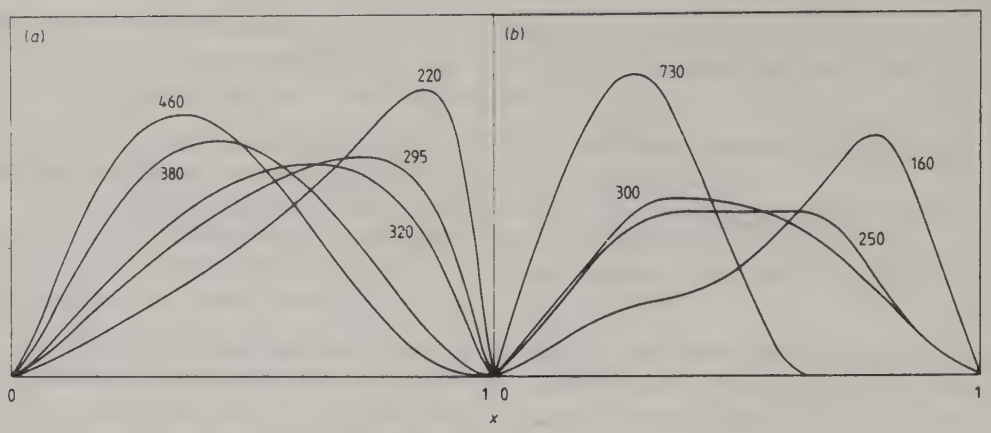


Figure 4. Temperature dependence of the distribution of quadrupolarisation $P(x)$ for samples with $X = (a)\ 0.53$, $(b)\ 0.37$. Temperatures are given on curves in mK.

$P(x)$ is zero for $x = 0$ since a finite value would result in a substantial sharp central line in the spectrum. The smoothness of $P(x)$ at $x = \frac{1}{2}$ implies that if $P(x)$ is non-zero for $x < 0$, it vanishes at $x = -\frac{1}{2}$ with a zero derivative which is possible. Thus negative quadrupolarisations may occur and moreover cannot be excluded on physical grounds.

(ii) $P(x)$ evolves only smoothly when the temperature is lowered. At intermediate temperatures the shape of $P(x)$ changes such that its maximum shifts towards larger values of x, as shown in figure 3. This evolution slows down progressively over a narrow temperature interval without any discernible discontinuity.

The as yet unexplained discrepancies between the spectra taken in different laboratories appear to be much less severe when one takes into account the extreme sensitivity of $S(\omega)$ to $P(x)$. The meaningful physical quantity is $P(x)$ rather than $S(\omega)$ and the overall features of experimental results do agree qualitatively when analysed in terms of the distribution $P(x)$. The differences that remain are of the order of what is shown in figure 2(b) and in all cases greater than that arising from the uncertainty of the fit even in the case of poorest precision (e.g. figure 3, part 1).

Of course, small details in $P(x)$ could in principle have some important physical meaning, but if one believes that the origin of $P(x)$ lies in the distribution of geometrical configurations of para-molecules ($J = 0$) among ortho-molecules ($J = 1$), then these details can easily be attributed to varying experimental procedures such as sample preparation and rate of cooling (Washburn *et al* 1982a). Furthermore, the peculiar properties of the transformation $P(x) \rightarrow S(\omega)$ prevent the direct detection of an eventual transition from some particular features of the spectra. For example the sudden apparition of the double-bump structure (see figure 3(b)) is simply caused by the flattening of $P(x)$ near its maximum.

Although there is no reason for the requirement of axial quadrupolarisations (hypothesis iii) to be completely satisfied, we believe that the overall shape and temperature evolution of the quadrupolarisation distribution would not be affected very much by a departure from axial symmetry of the local quadrupolarisations. Let us note that the broad width of $P(x)$ is not a characteristic feature of the glass regime as CW spectra for high concentrations already present departures from pure Pake doublets. It had already been suggested (Hardy and Berlinsky 1973) that a distribution of 'Pake

splittings' (referred to here as local quadrupolarisations) must be used in the interpretation of lineshapes. We have indeed carried out detailed analysis of lineshapes in the so-called long-range-ordered phase and have found distributions that, although not as broad as in the glass regime, clearly indicate that an interpretation in terms of a single order parameter (which would be extracted from some particular features of the spectra) is very crude and gives an oversimplified picture of the orientational transition.

4.2. The implications of the temperature dependence of $P(x)$ on the nature of the orientational ordering

In order to evaluate the degree of smoothness of the evolution of $P(x)$ in a quantitative fashion, we have compared its temperature dependence with what would be obtained for independent molecules sitting in a distribution of axially symmetric random quadrupolar fields (RQF). In this model, the quadrupolarisation for an ortho-molecule i is given by

$$x_i = (-e^{-\beta q_i/2} + e^{+\beta q_i})/(2e^{-\beta q_i/2} + e^{\beta q_i})$$

in which q_i is the amplitude of the random quadrupolar field acting on molecule i and β the inverse temperature. The virtue of this simple model is that the knowledge of $P(x)$ at one temperature is sufficient to reconstruct its entire temperature dependence. We have thus taken $P(x)$ at one intermediate temperature ($T = 320$ mK for $X = 0.53$) as the adjustable parameter for the comparison between experiment and the predictions of this model. The family of curves $P^{RQF}(x, T)$ for different temperatures is shown in figure 5 together with the curves deduced from lineshapes measurements. Both families of

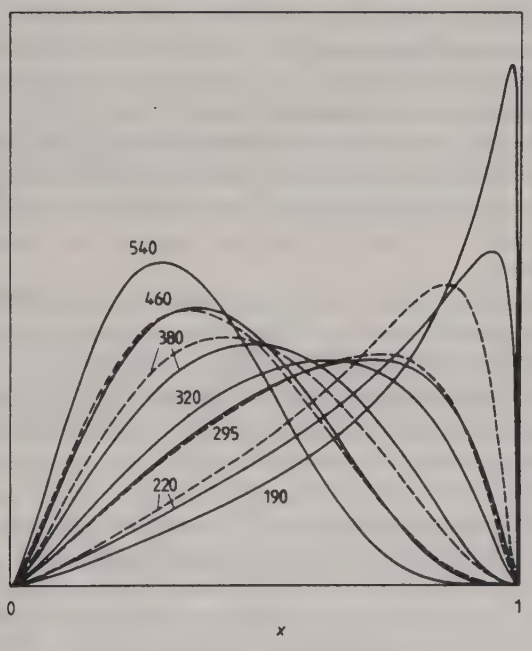


Figure 5. Comparison between the predictions of the RQF model for $X = 0.53$ for the evolution of $P(x)$ (full curve) and the experimental results (broken curve). The distribution of random fields has been chosen so that the calculated distribution $P(x)$ coincides with the experimental one at $T = 320$ mK. Temperatures are given in curves in mK.

curves have similar evolutions in the temperature range of 500–200 mK. This shows that in this range the freezing of molecular orientations is not more rapid than it is for a single-particle model.

At lower temperatures ($T < 200$ mK), the RQF model fails to explain the absence of any further evolution in $P(x)$. On the contrary, it predicts that $P(x)$ should become more and more strongly peaked at $x = 1$ as one approaches $T = 0$. The existence of the low-temperature regime where $P(x)$ is almost independent of temperature cannot be explained without assuming important quantum mechanical correlations between molecules. However, the crossover to this regime is insufficient to indicate the extent of the cooperativity of the freezing process. The RQF model can be refined to take into account quantum mechanical correlations, at the expense however of increased complexity. The refinement consists of considering, instead of an isolated molecule, a pair of molecules in a random field for which the quadrupolarisations can be calculated exactly. Another approach to a universal mapping for $P(x)$ has been developed by Candela *et al* (1981).

In summary, the orientations of ortho-molecules at intermediate concentrations become progressively more and more localised as the temperature decreases until a quantum regime, in which no further localisation occurs, is reached. This behaviour is very different from the sudden and almost complete localisation of orientations that is observed in pure ortho-hydrogen at the orientational transition.

4.3. The absence of any singularity in the temperature dependence of $P(x)$

Non-zero values of local quadrupolarisations exist at *all* temperatures in the hydrogen mixtures: the local quadrupolarisations cannot be taken here as the order parameters of a hypothetical glassy transition.

In order to clarify this point, let us compare the system of dilute quantum quadrupoles with the dilute ferro–antiferromagnets which can also form magnetic glasses at low T ($Eu_xSr_{1-x}S$ is the canonical example). In the latter system, the symmetry operation $S_i \rightarrow -S_i$ leaves the Hamiltonian in zero field invariant and therefore ensures that $\langle S_i \rangle = 0$ at sufficiently high temperatures. Such a symmetry operation does not exist in a system of quadrupoles and one expects non-vanishing quadrupolarisations at all temperatures except in the special case of a pure system with cubic symmetry. This case is realised in pure FCC ortho-hydrogen. In pure HCP ortho-hydrogen, local quadrupolarisations almost cancel to zero but are not expected to vanish completely on purely symmetry grounds.

In solid hydrogen, as soon as ortho-molecules convert into para ones, the crystal symmetry becomes imperfect and the above cancellation no longer occurs. The neighbouring molecules therefore develop some quadrupolarisation, even at high temperatures (Harris 1970). A high-temperature expansion up to second order gives $\frac{25}{18}\beta^2\Gamma^2$ for the local quadrupolarisations x_i around a para-molecule. This quadrupolarisation results from the combined effects on the anisotropy of the interaction and pair correlations between ortho-molecules around a para-molecule which is just a hole as far as orientational degrees of freedom are concerned. This effect somehow justifies the introduction of the RQF model which can reproduce it phenomenologically.

At low enough ortho-hydrogen concentrations, the quadrupolarisations due to the asymmetric environment of each molecule could be large enough to guide the system towards a well defined ground state and wash out any transition. The system would be somewhat similar to an antiferromagnet in an external field which would induce a magnetisation above the critical value at which the system ceases to show any transition.

The main difference here is that local quadrupolarisations are not induced by an external field but by the modification of the local symmetry at each site.

4.4. Further possibilities

Nevertheless, our results for the quadrupolarisation distribution do not exclude the possibility of a dynamical transition in the system. Recent measurements of the nuclear relaxation time T_1 (Sullivan and Estève 1981) have shown an important slowing down of the orientation fluctuations as the system approaches the regime for which $P(x)$ is almost independent of T. The large temperature dependence of T_1 strongly suggests a collective phenomenon in the slowing down of the orientational fluctuations. However, other experiments performed at Duke (Washburn *et al* 1982b) seem to be more compatible with a continuous freezing without any collective effect. Further experiments are now in progress to explore the spectrum of the orientational fluctuations in more detail.

5. Conclusion

NMR spectra of ortho–para mixtures below the critical concentration for long-range order have been quantitatively accounted for by a wide distribution of local quadrupolarisations. This distribution evolves with temperature in essentially the same manner for all samples studied.

(i) On cooling from high temperatures the initially narrow distribution broadens progressively while its overall weight is pulled towards higher quadrupolarisations.

(ii) This evolution slows down over a narrow temperature interval until a low-temperature regime is reached for which the distribution remains almost completely independent of temperature.

The picture that emerges from this temperature dependence is that of a continuous growth on each site of the local quadrupolarisation as T decreases until a limit, imposed by many particle quantum correlations, is reached. No indication of a sharp transition can be detected in the temperature dependence of the quadrupolarisation distribution.

Acknowledgments

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COMPLEMENTS

L'analyse présentée dans cet article repose sur l'hypothèse de quadrupolarisations axiales. Cette hypothèse est fausse à haute température (cf §.B.III) où les quadrupolarisations sont petites et n'est exacte dans la limite $T \to 0$ que pour des quadrupoles classiques. On ne sait pas dans quelle mesure la considération de quadrupolarisations non axiales ($\eta \neq 0$) permettrait aussi de rendre compte des spectres RMN. On peut néanmoins montrer [D82] que le second moment de la distribution de $\sqrt{\sigma^2+\eta^2}$ est alors le même que celui de P(x) et que les deux distributions sont identiques aux extrémités de leur intervalle de définition [0,1].

III - LES METHODES D'ECHOS ET LA DETECTION DES MOUVEMENTS DE ROTATION

1) Articles :

NMR PULSE STUDIES OF MOLECULAR SOLIDS $^{15}N_2$ AND H_2 :

- I SOLID ECHOES AND ORIENTATIONAL ORDERING
- II STIMULATED ECHOES AND SLOW ROTATIONAL MOTIONS

J. Phys. C: Solid State Phys., **15** (1982) 4881–4894. Printed in Great Britain

NMR pulse studies of molecular solids: $^{15}N_2$ and H_2: I. Solid echoes and orientational ordering

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Abstract. We develop a theory of solid echoes following a two-pulse RF sequence in orientationally ordered crystals such as solid $^{15}N_2$ and solid H_2 which takes into account the dipolar interactions between nuclei of different molecules. These interactions result in a damping of the solid echoes which is found to depend on the angle and axis of the rotation of the nuclear spins by the second pulse. The theoretical predictions are in quantitative agreement with the experimental results obtained both in solid $^{15}N_2$ and in solid H_2. We discuss the use of solid echoes for the study of orientational ordering in molecular solids, and in particular how one can take advantage of the unique possibility offered by these systems of suppressing the damping of solid echoes.

1. Introduction

In molecular solids, one has to consider two kinds of degrees of freedom: translational degrees of freedom for the centre-of-mass motion and orientational degrees of freedom for the rotational motion of the molecules.

When the isotropic intermolecular interactions are much stronger than the anisotropic contribution, there is at high temperature a solid phase in which the centres of mass of the molecules are essentially fixed at the lattice sites whereas the orientational degrees of freedom are not necessarily completely ordered (e.g. H_2, D_2, CO, C_2H_2, NH_3, BF_3, CH_4). The interest in these systems (Parsonage and Stavely 1978) lies in the great variety of phase transitions towards orientationally ordered phases that occur at lower temperatures. The simplest examples are provided by diatomic molecular solids such as H_2, D_2 and N_2 in which the orientational degrees of freedom (respectively those of 'quantum' and 'classical' rods) order under the effect of anisotropic interactions that are essentially quadrupolar (Silvera 1980, Scott 1976).

This paper is the first of a series devoted to the development of nuclear magnetic resonance (NMR) pulse methods designed to obtain a more detailed description of the orientational properties of these solids than is possible with the use of conventional NMR techniques. Apart from the investigation of the ordered phases, one of the important questions (for which little information has been obtained up to the present) that we address in these papers is how one can determine the manner in which orientational degrees of freedom become frozen at the phase transition towards an ordered phase.

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Nuclear magnetic resonance has played a major role in the investigation of these compounds and this has been mostly through the use of two methods: (i) the analysis of the NMR lineshapes and (ii) the analysis of the longitudinal relaxation times. We show here that spin echoes following a two-pulse sequence provide a more powerful means of looking at the fine structure of the lineshape, which depends on the orientational states of the molecules bearing the resonant nuclei, than the conventional continuous-wave technique. Spin echoes, then called solid echoes†, were observed in solid H_2 a long time ago (Metzger and Gaines 1966) but have only very recently been used to study the problem of orientational ordering (Cochran *et al* 1980). While the two-pulse response function of independent molecules is known, this is not the case when the dipolar interactions between nuclei of different molecules are also taken into account. These intermolecular interactions result in a broadening of the lineshape that limits the amount of information that can be obtained from it concerning the orientational states of the molecules. These interactions are also responsible for the damping of the solid echoes. The aim of this work is to provide a detailed understanding of this damping, to show that it can be almost completely removed for particular two-pulse sequences and then to explain how such undamped solid echoes may be exploited for studying the orientational ordering of diatomic molecules.

This paper is organised as follows. We first examine, in § 2, the time dependence of the nuclear operators and we then study the conditions for the focussing of solid echoes in § 3. A theoretical treatment of the damping of the echoes is given in § 4 and the predictions are confronted with the experimental results in § 5. Finally, we discuss the applications of solid echoes to the study of orientational ordering in § 6.

2. NMR and orientational ordering of diatomic molecules

Since H_2 and N_2 molecules are composed of identical fermions ($i = \frac{1}{2}$), there are two molecular species: (i) para-molecules with total nuclear spin quantum number $I = 0$ and an even-symmetry orbital wavefunction; (ii) ortho-molecules with $I = 1$ and an odd-symmetry orbital wavefunction. In NMR experiments one observes only the ortho-molecules. As the conversion rate in the solid phase is very slow, we shall neglect its effect on the time scale of our experiments.

The ability of NMR to probe the molecular orientations lies in the dependence of the nuclear Hamiltonian on the angles Θ_i between the molecular axes and the $\hat{Z}$ axis along which the field is applied (Schweizer *et al* 1979). More precisely, the secular part of the dipolar Hamiltonian of nuclei belonging to the same ortho-molecule i is given by

$$H'_{D_i}(t) = -(\hbar D/3)\langle P_2(\Theta_i)\rangle_Q(t)(3I_{z_i}^2 - 2) \tag{1}$$

where the brackets $\langle \ldots \rangle_Q$ denote a quantum average over the orbital state of the molecule i. ($P_2(\Theta_i)$ is the conventional Legendre polynomial.)

We shall assume, as has always been observed, that the orientational state of each molecule i has a symmetry axis $\hat{\zeta}_i$ (making an angle γ_i with the molecular axis and θ_i with the $\hat{Z}$ axis) around which the molecule performs a rotational motion at a characteristic frequency ω_R much greater than the dipolar frequency D (extreme-narrowing regime). It then follows using the addition theorem for spherical harmonics that the relevant

† These echoes are similar to Soloman's quadrupolar echoes (Abragam 1961).

Hamiltonian H'_{D_i} for NMR is

$$H'_{D_i} = -(\hbar D/3)\, P_2(\theta_i)\, p_i(3I_{z_i}^2 - 2) \tag{2}$$

where p_i represents a time average of $\langle P_2(\gamma_i)\rangle_Q(t)$ performed on a time long compared with D^{-1}. p_i is the orientational order parameter of the molecule i. The set of angles and order parameters $\{\theta_i, p_i\}$ fully specifies the system from the NMR point of view. For molecules in well defined orientational states these parameters are time-independent†, but we shall also consider the case where orientational states of the molecules evolve for which the θ_i and p_i have to be considered as functions of time.

The intramolecular dipolar Hamiltonian of the system is then given by

$$H'_D = -\hbar(\tfrac{2}{3})^{1/2} \sum_i D_i I_{i0}^2 \tag{3}$$

with

$$D_i = DP_2(\theta_i)p_i \qquad D = \tfrac{3}{2}\gamma^2\hbar/R^3 \qquad I_{i0}^2 = (3I_{z_i}^2 - 2)/6^{1/2}$$

$$D_{H_2} = 1359 \times 10^3 \text{ rad s}^{-1} \qquad D_{N_2} = 8710 \text{ rad s}^{-1}.$$

For N_2 molecules, one also has an anisotropic chemical shift Hamiltonian (Ishol and Scott 1977). Its secular part is

$$H'_{\chi_i} = -\hbar\chi_i I_{z_i} \qquad \text{with } \chi_i = (4 \times 10^{-6})\omega_0 P_2(\theta_i)p_i. \tag{4}$$

The degeneracy of the NMR frequencies corresponding to the transitions $I_z = 1 \rightarrow 0$ and $I_z = 0 \rightarrow -1$ is therefore slightly lifted according to

$$\omega_i(\pm) = \omega_0 - (\chi_i \pm D_i). \tag{5}$$

We shall consider firstly the time evolution of the nuclear spin operators under the effect of the intramolecular Hamiltonian in the rotating frame ($\omega = \omega_0 + \Delta\omega$):

$$H_i^0 = -\hbar\Delta\omega I_{z_i} + H'_{D_i} + H'_{\chi_i} \tag{6}$$

in which a slight departure $\Delta\omega$ from resonance has been introduced. The time evolution of a complete set of irreducible tensorial operators $I_{iQ}^K(t)$ (rank K, component Q) is readily calculated (see table 1). As the Hamiltonian H_i^0 commutes with I_{z_i}, the quantum number Q is conserved during the evolution. This is not the case for K, since H_i^0 is not purely vectorial.

Table 1. Time evolution of a complete set of irreducible tensorial operators generated by the intramolecular Hamiltonian.

Tensorial operator I_Q^K	Time dependence $I_{iQ}^K(t)$
$K=1$ $\begin{cases} I_0^1 = 2^{-1/2}I_z \\ I_{\pm1}^1 = \mp\frac{1}{2}(I_x \pm iI_y) \end{cases}$	$\begin{cases} I_{i0}^1(t) = I_{i0}^1 \\ I_{i\pm1}^1(t) = e^{\pm i\chi_i t}\cos D_i t I_{i\pm1}^1 \mp i \sin D_i t\, e^{\pm i\chi_i t} I_{i\pm1}^2 \end{cases}$
$K=2$ $\begin{cases} I_0^2 = 6^{-1/2}(3I_z^2 - 2) \\ I_{\pm1}^2 = \mp\frac{1}{2}(I_\pm I_z + I_z I_\pm) \\ I_{\pm2}^2 = I_\pm^2/2 \end{cases}$	$\begin{cases} I_{i0}^2(t) = I_{i0}^2 \\ I_{i\pm1}^2(t) = \mp ie^{\pm i\chi_i t}\sin D_i t I_{i\pm1}^1 + e^{\pm i\chi_i t}\cos D_i t I_{i\pm1}^2 \\ I_{i\pm2}^2(t) = e^{\pm 2i\chi_i t} I_{i\pm2}^2 \end{cases}$

† p_i is then the thermodynamic average $\langle P_2(\gamma)\rangle_T$.

We now introduce the intermolecular dipolar interactions. Since the intermolecular distances are much greater than the distance between nuclei of the same molecule, we shall take for the dipolar Hamiltonian the same expression as for ($I = 1$) nuclei localised at the centres of gravity of the molecules. Its secular part H_d may be split into two terms, H'_d and H''_d, in such a way that H'_d is the secular part of the dipolar Hamiltonian with respect to both the Zeeman Hamiltonian (i.e. $[H'_d, \Sigma_i I_{z_i}] = 0$) and the intramolecular Hamiltonian $(H^0)_i$ (i.e. $[H'_d, I_{z_i}] = 0$ for all i). This determines H'_d and H''_d:

$$H'_d = -\sum_{(i,j)} \hbar d_{ij} I_{z_i} I_{z_j} \tag{7}$$

$$H''_d = \sum_{(i,j)} \frac{\hbar d_{ij}}{4} (I_{+i} I_{-j} + I_{-i} I_{+j}) \tag{7'}$$

with

$$d_{ij} = \gamma^2 \hbar (3 \cos^2 \theta_{ij} - 1)/r_{ij}^3.$$

In these systems, neighbouring molecules always have different orientations in the ordered phase (Raich and Etters 1968, Sullivan *et al* 1978), and their NMR frequencies differ by an amount of the order of D which is much greater than d_{ij} ($D/d > 10$). One says that the nuclei are not on 'speaking terms'. The flip-flop transitions induced by H''_d are therefore almost completely quenched since they do not conserve the intramolecular energy†. This key point is carefully checked in paper II (Sullivan *et al* 1982), where we investigate the decay of stimulated echoes when they are damped only by the transitions induced by H''_d. The relevant Hamiltonian in the rotating frame is therefore

$$H = H^0 + H'_d = -\hbar \sum_i [(\Delta\omega + \chi_i) I_{z_i} + D_i (\tfrac{2}{3})^{1/2} I_{i0}^2] - \hbar \sum_{(i,j)} d_{ij} I_{z_i} I_{z_j}. \tag{8}$$

We now calculate the time evolution of the operators I_{iQ}^K under the effect of the complete Hamiltonian (8):

$$\mathbb{I}_{iQ}^K(t) = \exp[-(\mathrm{i}/\hbar)(H^0 + H'_d)t]\, I_{iQ}^K \exp[(\mathrm{i}/\hbar)(H^0 + H'_d)t]. \tag{9}$$

Since H^0 and H'_d commute, $I_Q^K(t)$ may be written in the following form:

$$\mathbb{I}_{iQ}^K(t) = \exp[-(\mathrm{i}/\hbar)H^0 t]\{\exp[-(\mathrm{i}/\hbar)H'_d\, \mathrm{d}t]\, I_{iQ}^K \exp[(\mathrm{i}/\hbar)H'_d\, \mathrm{d}t]\} \exp[(\mathrm{i}/\hbar)H^0 t]. \tag{10}$$

The section in curly brackets is analogous to the transformation of I_{iQ}^K under the effect of a rotation of the $\hat{Z}$ axis by an 'angle' $(\Sigma_j d_{ij} I_{z_j} t)$. This rotation angle is an operator, but the usual transformation formula for a real angle still holds (as may be easily checked using a series expansion) and one has

$$[\exp(-\mathrm{i}/\hbar' H'_d\, \mathrm{d}t) I_{iQ}^K \exp(\mathrm{i}/\hbar' H'_d\, \mathrm{d}t)] = \exp(\mathrm{i}Qt \sum_j d_{ij} I_{z_j})\, I_{iQ}^K. \tag{11}$$

Since H^0 commutes with the I_{z_j}, it follows from (10) and (11) that

$$\mathbb{I}_{iQ}^K(t) = \exp(\mathrm{i}Qt \sum_j d_{ij} I_{z_j})\, I_{iQ}^K(t). \tag{12}$$

The effect of H'_d results in a phase shift of 'angle' $(Qt \Sigma_j d_{ij} I_{z_j})$.

† In the Pa_3 structure realised in N_2 and in pure ortho H_2, next-nearest-neighbouring (NNN) molecules have similar orientations. Flip-flop transitions induced by their weak dipolar interactions ($d_{NNN}/d_{NN} \simeq \frac{1}{10}$) would therefor be expected. In fact, these transitions are in their turn quenched since they do not conserve the dipolar energy between nearest-neighbouring spins by an amount $\simeq d_{NN}$ which is much greater than d_{NNN}.

3. Formation of solid echoes

We establish here the full expression of the transient signal following a general two-pulse sequence denoted by $(\pi/2 - \tau - \psi_\varphi)$ as sketched in figure 1. Solid echoes originate in the compensation of the evolution operators between t: $0 \rightarrow \tau$ and t: $\tau \rightarrow 2\tau$.

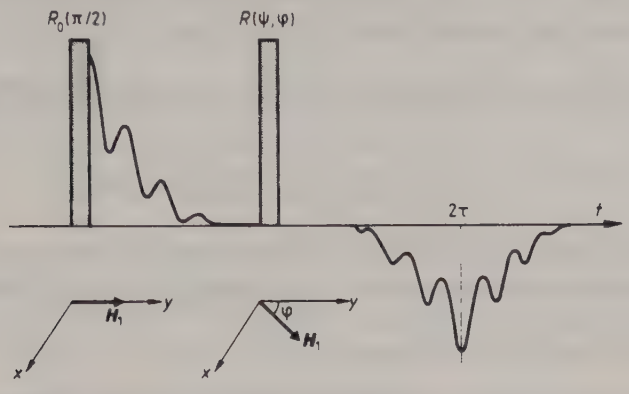

Figure 1. Formation of a solid echo following two RF pulses separated by a time τ. The second pulse corresponds to a rotation of angle ψ around the direction of the field $\boldsymbol{H}_1$ in the rotating frame. This sequence is referred to as a $(\pi/2 - \tau - \psi_\varphi)$ sequence in the text.

The first pulse R_0 puts the magnetisation along the $\hat{x}$ axis. It transforms the equilibrium density matrix

$$\rho_{eq} = [\mathbf{1} + (\hbar\omega_0/kT)I_z] \qquad \text{into} \qquad R_0\rho_{eq}R_0^\dagger = [\mathbf{1} + (\hbar\omega_0/kT)I_x].$$

We consider then the subsequent evolution of the normalised density matrix $\rho(t = 0^+) = I_x$. Just after the second pulse $R(\psi, \varphi)$, which occurs at time τ, $\rho(\tau^+)$ is given by

$$\rho(\tau^+) = R\mathbb{I}_x(\tau)R^\dagger. \tag{13}$$

The density matrix at time t' after the second pulse is therefore

$$\rho(t') = \exp[-(i/\hbar)Ht']\,\rho(\tau^+)\exp[(i/\hbar)Ht'] \tag{14}$$

and the signal $S_i(t')$ received in the NMR coil is given by

$$S_i(t') = S_{x_i}(t') + iS_{y_i}(t') = \mathrm{Tr}(\rho(t')I_{+_i})/\mathrm{Tr}\,I_{x_i}^2. \tag{15}$$

Using the cyclic invariance of the trace, $S_i(t')$ may be written in the more convenient form

$$S_i(t') = \mathrm{Tr}\left[R\left(\sum_j \mathbb{I}_{x_j}(\tau)\right)R^\dagger\mathbb{I}_{+_i}(-t')\right](\mathrm{Tr}\,I_{x_i}^2)^{-1}. \tag{16}$$

Let us first calculate the signal $\mathcal{S}_i(t')$ obtained at resonance when the intermolecular interactions are not taken into account. In this case, the only term that contributes to (16) is obtained by picking $\mathbb{I}_{x_i}(\tau)$ in $(\Sigma_j\,\mathbb{I}_{x_j}(\tau))$. The expression of $I_{x_i}(\tau)$ is easily extracted from table 1. The pulse R then rotates the I_Q^K of given K amongst themselves according

to

$$RI_Q^K R^+ = \Sigma\, d_{Q'Q}^{(K)} I_{Q'}^K. \tag{17}$$

In order to calculate $\mathcal{S}_i(t')$ it is sufficient to know the terms with $Q = -1$ in $\rho(\tau^+)$, since all other terms do not contribute to the trace (16) by virtue of the orthogonality relations $\mathrm{Tr}\, I_Q^K I_{Q'}^K = (-1)^Q \delta_{QQ'}$. Having in view more complicated pulse sequences (see paper II), we also give the terms with $Q = 0$ in $\rho_i(\tau^+)$:

$$\begin{cases} \rho_i(\tau^+)_{Q=-1} = \cos(D_i\tau)[\cos^2(\psi/2)\, e^{-i\chi_i\tau} - \sin^2(\psi/2)\, e^{i\chi_i\tau} e^{2i\varphi}]\, I_{i1}^1 \\ \qquad + [i \sin(D_i\tau)/2][(1 + \cos\psi)(2\cos\psi - 1)\, e^{-i\chi_i\tau} \\ \qquad + (1 - \cos\psi)(2\cos\psi + 1)\, e^{i\chi_i\tau} e^{2i\varphi}]\, I_{i1}^2 \qquad (18) \\ \rho_i(\tau^+)_{Q=0} = -\cos(D_i\tau)\, 2^{1/2} \sin\psi \cos(\chi_i\tau - \varphi)\, I_{i0}^1 \\ \qquad + \sin(D_i\tau)\, 6^{1/2} \sin\psi \cos\psi \sin(\chi_i\tau + \varphi)\, I_{i0}^2. \qquad (19) \end{cases}$$

One finds then for the signal (16) $\mathcal{S}_i(t')$

$$\mathcal{S}_i(t') = e^{2i\varphi}\, U_i(t') + V_i(t') \tag{20}$$

with

$$U_i(t') = -(\sin^2\psi/2)[e^{-i\chi_i(t'-\tau)} \cos D_i(t' - \tau)] + [\cos\psi(1 - \cos\psi)/2][e^{-i\chi_i(t'-\tau)} \cos D_i(t' + \tau)] \tag{20'}$$

$$V_i(t') = (\sin^2\psi/2)[e^{-i\chi_i(t'+\tau)} \cos D_i(t' - \tau)] + [\cos\psi(1 + \cos\psi)/2][e^{-i\chi_i(t'+\tau)} \cos D_i(t' + \tau)]. \tag{20''}$$

For a wide distribution of orientational states (and hence of values of D_i and χ_i), these expressions clearly exhibit the formation of a solid echo by the focussing of the transverse magnetisation at time $t' = \tau$. The amplitude of the signal $\mathcal{S}(t')$ at $t' = \tau$ is given by

$$\mathcal{S}(t') = \subset \mathcal{S}_i(t' = \tau) \supset = (e^{2i\varphi}/2)[-\sin^2\psi + \cos\psi(1 - \cos\psi) \subset \cos 2D_i\tau \supset] + \tfrac{1}{2}[\sin^2\psi \subset e^{-2i\chi_i\tau} \supset + \cos\psi(1 + \cos\psi) \subset e^{-2i\chi_i\tau} \cos 2D_i\tau \supset] \tag{21}$$

where the brackets $\subset \ldots \supset$ refer to an average over the different molecules i. For N_2 molecules, when the conditions $D\tau \gg 1$ and $\chi\tau \gg 1$ are fulfilled, the solid-echo amplitude is simply $\mathcal{S}(\tau) = -e^{2i\varphi}(\sin^2\psi)/2$. For H_2 molecules, both terms of expression (21) contribute (since $\chi = 0$ implies $\subset e^{-2i\chi_i\tau} \supset = 1$) and one has $\mathcal{S}(\tau) = (1 - e^{2i\varphi})(\sin^2\psi)/2$. Relation (21) also shows how the amplitude of the signal $\mathcal{S}(\tau)$ can be used to determine $\subset \cos 2D_i\tau \supset$ or $\subset e^{-2i\chi_i\tau} \supset$ and in this way obtain information concerning the orientational states of the molecules. Before developing this any further (§ 6) it is necessary to understand the effect of the intermolecular interactions on the solid echoes.

4. Damping of solid echoes by intermolecular dipolar interactions

We calculate here the signal $S(t')$ given by (16) when the complete Hamiltonian (8) is taken into account. 'Unlike' terms in (16) of the form $\mathrm{Tr}(R\mathbb{I}_{x_i}(\tau)\, R^+\mathbb{I}_{+_j}(-t))/\mathrm{Tr}\, I_{x_i}^2$ with $j \neq i$ no longer vanish. They are nevertheless very small and we have checked that they

make a negligible contribution to the solid echoes in our systems. The expressions of the operators appearing in the 'like' terms are deduced from (12):

$$\mathbb{I}_{x_i}(\tau) = \cos \delta_i \tau I_{x_i}(\tau) - \sin \delta_i \tau I_{y_i}(\tau) \tag{22}$$

$$\mathbb{I}_{+_i}(-t') = e^{-i\delta_i t'} I_{+_i}(-t') \tag{22'}$$

with $\delta_i = \Sigma_j d_{ij} I_{z_j}$.

The trace operation involved in (16) can then be written in the following form:

$$S_i(t') = \left[\operatorname*{Tr}_i (R I_{x_i}(\tau) R^\dagger I_{+_i}(-t')) / \operatorname*{Tr}_i I_x^2 \right] \left\{ \operatorname*{Tr}_{j \neq i} (R \cos \delta_i \tau R^\dagger e^{-i\delta_i t'}) / \operatorname*{Tr}_{j \neq i} \mathbf{1} \right\}$$
$$+ \left[\operatorname*{Tr}_i (R I_{y_i}(\tau) R^\dagger I_{+_i}(-t')) / \operatorname*{Tr}_i I_x^2 \right] \left\{ \operatorname*{Tr}_{j \neq i} [R(-\sin \delta_i \tau) R^\dagger e^{-i\delta_i t'}] / \operatorname*{Tr}_{j \neq i} \mathbf{1} \right\}. \tag{23}$$

The first expression in square brackets is just the signal $\mathcal{S}_i(t')$. The second one corresponds to the signal $\mathcal{S}_{i_y}(t')$ that would be obtained if the magnetisation just after the first pulse were along the $\hat{y}$ axis. Considering a frame rotated by $\pi/2$ around the $\hat{z}$ axis (so that $\hat{x}' = \hat{y}$), one obtains the relation

$$\mathcal{S}_{i_y}(t') = i\mathcal{S}_i(t') | \varphi' = \varphi - \pi/2. \tag{24}$$

It then follows from (20) that

$$\mathcal{S}_{i_y}(t') = -i\, e^{2i\varphi} U_i(t') + iV(t'). \tag{25}$$

By using (25) in (23), we find

$$S_i(t') = e^{2i\varphi} U_i(t') \mathcal{F}_{i+} + V_i(t') \mathcal{F}_{i-} \tag{26}$$

with:

$$\mathcal{F}_{i\pm} = \operatorname*{Tr}_{j \neq i} (R\, e^{\pm i\delta_i \tau} R^\dagger e^{-i\delta_i t'}) / \operatorname*{Tr}_{j \neq i} \mathbf{1}. \tag{26'}$$

As expected, the introduction of H_d' results in a damping of the solid-echo amplitude. More unexpectedly, the damping is not the same for all terms of $S_i(t')$ and it depends on the rotation angle ψ of the second pulse. We calculate here the damping factors $\mathcal{F}_{i\pm}$ at time $t' = \tau$ in order to determine how the signal amplitude (21) has to be modified. The expression (26') of $\mathcal{F}_{i\pm}$ may be factorised according to

$$\mathcal{F}_{i\pm} = \prod_{j \neq i} f_{ij\pm} = \prod_{j \neq i} \left\{ \operatorname*{Tr}_j [R \exp(\pm i d_{ij} \tau I_{z_j}) R^\dagger \exp(-i d_{ij} \tau I_{zj})] / \operatorname*{Tr}_j \mathbf{1} \right\}. \tag{27}$$

One has to calculate the trace of a product of rotation operators, which is still a rotation operator $R'_\pm$. This requires only that one knows the rotation angle $\Gamma_\pm$ of $R'_\pm$ since its trace is given by

$$\operatorname*{Tr}_j R'_\pm = (1 + 2 \cos \Gamma_\pm). \tag{28}$$

It is convenient to calculate Γ by using the representation of the rotation group in the manifold ($J = \frac{1}{2}$). In this way one obtains, after some algebra,

$$|\sin \Gamma_+/4| = |(\sin \psi/2) \sin d_{ij}\tau/2| \tag{29}$$

$$|\sin \Gamma_-/4| = |(\cos \psi/2) \sin d_{ij}\tau/2|. \tag{29'}$$

(These relations determine cos Γ without any ambiguity.) One deduces from these expressions the following symmetry relation:

$$\mathcal{F}_{i+}(\psi, \tau) = \mathcal{F}_{i-}(\pi - \psi, \tau) \tag{30}$$

which implies, for $\psi = \pi/2$,

$$\mathcal{F}_{i+}(\pi/2, \tau) = \mathcal{F}_{i-}(\pi/2, \tau). \tag{30'}$$

If the Hamiltonian is purely dipolar ($\chi = 0$) this last relation leads to the well known result that the echo (26) vanishes for $\varphi = 0$, $\psi = \pi/2$. On the other hand when there is a chemical shift ($\chi \neq 0$) the echo does *not* vanish for $\varphi = 0$, $\psi = \pi/2$.

The relation (30) also reveals a more striking feature: *the damping may be suppressed* for special angles (at least to within the excellent approximation considered here that flip-flop terms of H_d'' may be completely ignored), since (27), (28), (29) and (29') imply

$$f_{ij+}(\psi = 0, \tau) = f_{ij-}(\psi = \pi, \tau) = 1 \tag{31}$$

and hence

$$\mathcal{F}_{i+}(\psi = 0, \tau) = \mathcal{F}_{i-}(\psi = \pi, \tau) = 1. \tag{31'}$$

A closed form for the damping factors $\mathcal{F}_{\pm}$ cannot be obtained without approximations. For times τ sufficiently short that $d_{ij}\tau/2 \ll 2\pi$, we can use the following approximations in expressions (29) and (29'):

$$\Gamma_{ij+}/4 \simeq (\sin \psi/2) d_{ij}\tau/2 \qquad \Gamma_{ij-}/4 \simeq (\cos \psi/2)\, d_{ij}\tau/2 \tag{32}$$

which leads to the following expression for the $\mathcal{F}$:

$$\mathcal{F}_{i+} \simeq \prod_j \frac{1 + 2\cos(2d_{ij}\tau \sin \psi/2)}{3} \tag{33}$$

$$\mathcal{F}_{i-} \simeq \prod_j \frac{1 + 2\cos(2d_{ij}\tau \cos \psi/2)}{3}. \tag{33'}$$

Within this approximation, the damping factors $\mathcal{F}_+$ and $\mathcal{F}_-$ depend only on ($\tau \sin \psi/2$) and ($\tau \cos \psi/2$), respectively.

5. Experimental study of solid echoes

We have studied solid echoes in $^{15}N_2$ and H_2 powdered samples using a coherent detection of the transient signals.

5.1. Solid echoes in $^{15}N_2$

Our pulse spectrometer was operated at a Larmor frequency $\nu_0 \simeq 3$ MHz, and the duration of the RF pulses was less than 15 μs for $\pi/2$ rotations. The signals were stored in a multichannel analyser and accumulated to improve the signal-to-noise ratio when necessary.

For times such that $D\tau \gg 1$ and $\chi\tau \gg 1$, the previous theory predicts a solid-echo amplitude (26) given by

$$S(\tau) = -(e^{2i\varphi}/2) \sin^2\psi \mathcal{F}_+(\psi, \tau) \qquad \text{with } \mathcal{F}_+ = \subset\mathcal{F}_{i+}\supset. \tag{34}$$

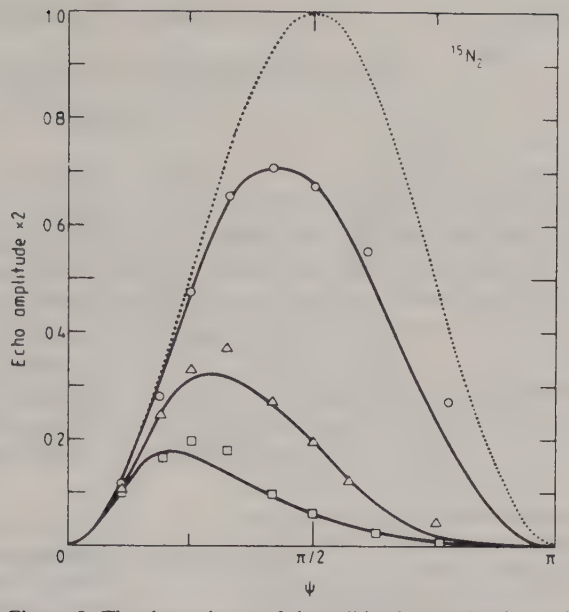

Figure 2. The dependence of the solid-echo amplitude on the angle of rotation ψ of the second pulse for various times 2τ: $2\tau = 5.4$ ms (circles); 9 ms (triangles); 13 ms (squares). The full curves are obtained by assuming that the damping factor $\mathcal{F}_+$ depends only on $\tau \sin \psi/2$ and using its measured value for $\psi = \pi/2$. The dotted curve represents the function $\sin^2\psi$.

The variations of $S(\tau)$ with ψ are shown in figure 2 for different values of τ. As predicted, the damping factor depends on ψ, the effect becoming more pronounced as one increases τ. Moreover, the dependence of the damping factor on $(\tau \sin \psi/2)$ only is well verified: the full curves in figure 2 have been deduced from the measured damping factor for $\psi = \pi/2$ and by assuming that the damping depends only on $(\tau \sin \psi/2)$.

The experimental decay of $S(\tau)$ on increasing τ always has the same behaviour as shown in figure 3 for the case $\psi = \pi/2$: an exponential regime is reached when the damping factor is less than 0.75. The dependence of the related relaxation rates T_2^{-1} on ψ is compared in figure 4 with the law $T_2^{-1} \propto \sin \psi/2$. Slight deviations are observed at small angles ψ for which the approximation (32) breaks down before the decay is almost complete.

We have also computed numerically the expression (33′) of the damping factor $\mathcal{F}_+(\psi = \pi/2, \tau)$ and performed a powder average. The result (the dotted curve in figure 3) is in close agreement with the measured damping factor.

5.2. Solid echoes in H_2

The absence of the anisotropic chemical shift in solid H_2 allows one to test features of the above theory that are not immediately accessible with experiments on solid $^{15}N_2$.

Experiments were conducted on a H_2 sample having an ortho concentration 45% at a temperature of 250 mK, for which the orientational states are frozen, at least on the time scale of our experiments (Sullivan *et al* 1978). The Larmor frequency was $\nu_0 \simeq 25$ MHz, and $\pi/2$ rotations were achieved in approximately 0.8 μs.

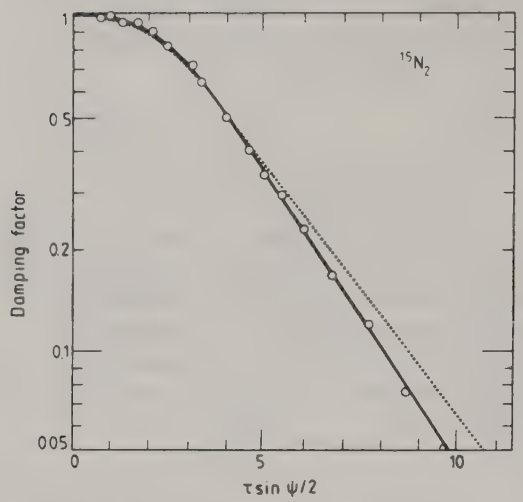

Figure 3. Measured damping factor $\mathcal{F}_+(\tau)$ against $\tau \sin \psi/2$ (full curve). τ is in ms. The damping factor $\mathcal{F}_+$ calculated in the short-time approximation (32), (33′) is given by the dotted curve.

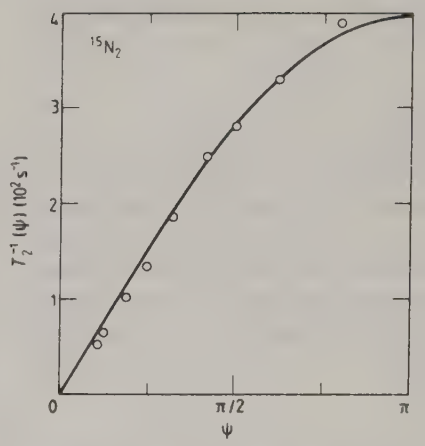

Figure 4. Dependence of the relaxation rate T_2^{-1} in the exponential regime (long-time dependence of figure 3) as a function of the rotation angle ψ. The full curve represents the fit $T_2^{-1}(\psi) = 4 \times 10^2 \sin \psi/2$ (s^{-1}).

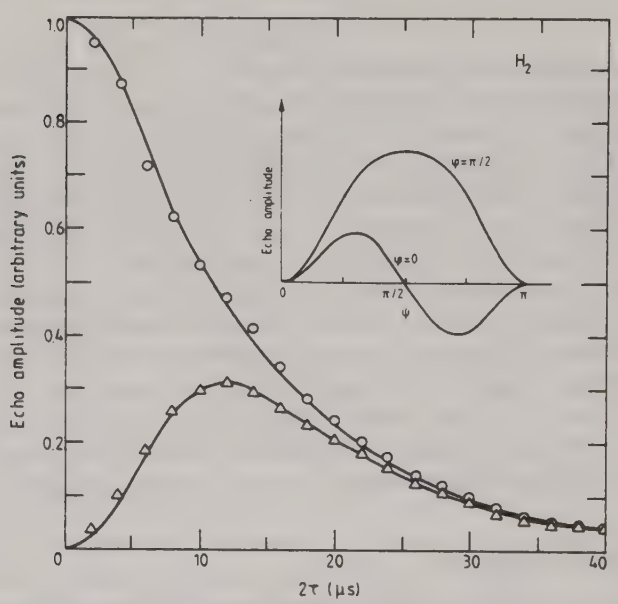

Figure 5. Damping of the solid-echo amplitude $S(\tau)$ in solid H_2 for: $|S(\tau, \psi = 2\pi/9, \varphi = \pi/2)| = \frac{1}{2}(\mathcal{F}_+ + \mathcal{F}_-)$ (circles); $|S(\tau, \psi = 2\pi/9, \varphi = 0)| = \frac{1}{2}(\mathcal{F}_+ - \mathcal{F}_-)$ (triangles). The full curves have been obtained using the damping factor $\mathcal{F}_+(\tau, \psi = \pi/2)$ measured in $^{15}N_2$ corrected by a scaling factor to account for the ratio of the strengths of the intermolecular interactions in H_2 and $^{15}N_2$. The dependence of the echo amplitude on ψ for phases $\varphi = \pi/2$ and $\varphi = 0$ is shown in the inset for a value of τ such that $\mathcal{F}_+(\pi/2, \tau)$ is e^{-1}.

For $D\tau \gg 1$, the solid-echo amplitude (26) reduces to

$$S(\tau) = -\tfrac{1}{2}(\sin^2\psi)(e^{2i\varphi}\mathcal{F}_+ - \mathcal{F}_-). \tag{35}$$

As stressed above the echo vanishes for $\varphi = 0$, $\psi = \pi/2$. We have studied the echo decay in the cases ($\psi = 2\pi/9$, $\varphi = 0$) and ($\psi = 2\pi/9$, $\varphi = \pi/2$). The existence of a solid echo for $\varphi = 0$ originates only in the difference between the damping factors $\mathcal{F}_+$ and $\mathcal{F}_-$. Its experimental observation therefore provides a nice check of the theory. Furthermore, the time dependence of both echoes, as shown in figure 5, agrees with the expected one deduced from the measured damping function $\mathcal{F}_+$ in $^{15}N_2$ corrected by the appropriate scaling factor.

These results for both solid N_2 and solid H_2 show that our treatment of solid echoes based on the quenching of flip-flop transitions induced by the non secular term H_d'' is in very good agreement with experimental facts.

6. Solid echoes and orientational ordering

We discuss here the different ways in which solid echoes may be used for the determination of the orientational states of the molecules. When the intermolecular dipolar interactions are taken into account, the expression (21) of the signal at time $t' = \tau$ has to be modified according to†

$$\begin{aligned} S(\tau, \psi, \varphi) = (e^{2i\varphi}/2)[-\sin^2\psi + \cos\psi(1 - \cos\psi) \subset \cos 2D_i\tau \supset]\,\mathcal{F}_+(\psi, \tau) \\ + \tfrac{1}{2}[\sin^2\psi \subset e^{-2i\chi_i\tau} \supset + \cos\psi(1 + \cos\psi) \\ \subset e^{-2i\chi_i\tau}\cos 2D_i\tau \supset]\mathcal{F}_-(\psi, \tau). \end{aligned} \tag{36}$$

An interesting quantity to measure in orientational studies is $\subset \cos 2D_i\tau \supset$, since it is directly related to the molecular order parameters. This term is easily extracted from the signals $S(\tau)$ obtained for ($\psi = \pi$, $\varphi = 0$).

As the damping factor $\mathcal{F}_+(\psi, \tau)$ decreases on increasing ψ, it is more convenient to perform a second pulse of small angle ψ in order to take advantage of a damping factor close to unity. In the limit $\psi \to 0$ the damping is suppressed, but the factor $\cos\psi(1 - \cos\psi)$ goes to zero. A compromise has to be found between a sufficiently intense signal and high resolution. The result for $\psi = \pi/6$ is shown in figure 6: the small modulation originating in the beats of $\subset \cos 2D_i\tau \supset$ is far less damped than the free induction decay signal (whose damping factor at time t is equal to $\mathcal{F}_+(\psi = \pi, \tau = t/2)$). This method is equivalent to that of observing the dipolar lineshape structure without the broadening originating in the intermolecular dipolar interactions. This is a rather unique situation in NMR.

In the case of a small order parameter, or when neighbouring molecules have similar orientational states, our treatment of the intermolecular interactions breaks down since flip-flop transitions may occur without an energy imbalance greater than the strength d of H_d''. The quantity $\subset \cos 2D_i\tau \supset$ may nevertheless be estimated if its decay takes place in a time of order d^{-1}. We have in this way measured the small residual order parameter in the orientationally disordered phase of solid $^{15}N_2$, for which the lineshape was of little use (Estève and Sullivan 1982).

† We neglect here any correlation between D_i (which depends on the angle between $\hat{\xi}_i$ and $\hat{Z}_i$) and $\mathcal{F}_i$ (which depends on the orientation of the crystal to which the molecule i belongs).

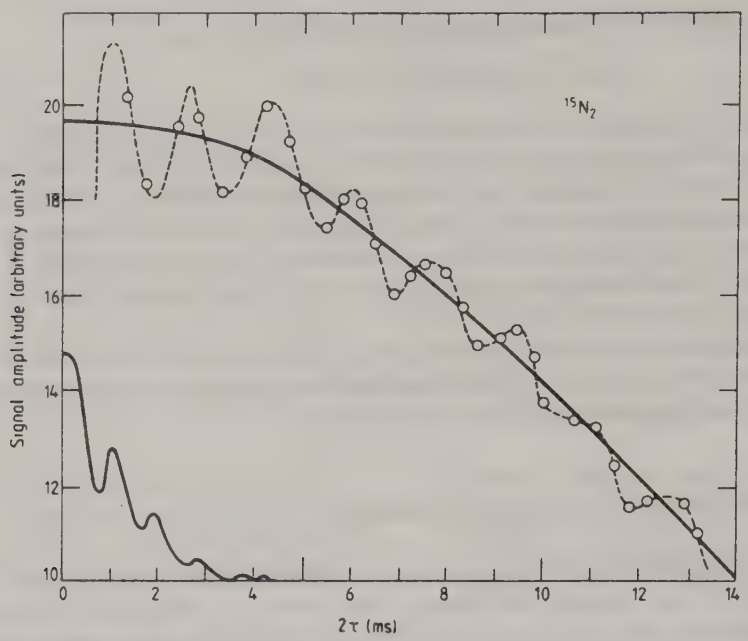

Figure 6. Modulation of the signal $|S(\tau, \psi = \pi/6, \varphi = 0) - S(\tau, \psi = \pi/6, \varphi = \pi/2)|$ in solid $^{15}N_2$ due to the non-vanishing term $\propto \subset \cos 2D_i\tau \supset$. The beats of $\subset \cos 2D_i\tau \supset$ are far less damped than those appearing in the free induction decay (full curve) as a result of the suppression of the damping when the rotation angle ψ goes toward zero.

We now discuss the behaviour of solid echoes when the orientational states are not completely fixed, but evolve at a characteristic motional frequency ω_m. When the time $\tau_m = \omega_m^{-1}$ characterising the motion becomes greater than D^{-1}, the lineshape broadens and its fine structure evolves until it reaches its rigid-lattice shape (Abragam 1961). In this regime, the lineshape (or the free induction decay (FID)) is rather difficult to use for gaining information concerning the motion, since its fine structure depends both on the statistical distribution of the order parameters and on their time evolution. Solid echoes are better adapted to this task since (i) their amplitude is only affected by the variations of the order parameters and not by their statistical distribution and (ii) they are (for small angles ψ) less damped than the FID signals.

When the set of variables $\{\theta_i, p_i\}$ specifying the intramolecular nuclear Hamiltonian varies with time, the evolution operator between t and $t + \Delta t$ is given by

$$U(t, t + \Delta t) = \exp\left(-i/\hbar \int_t^{t+\Delta t} H(t'')\, dt''\right). \tag{37}$$

We shall consider here the case of H_2 ($\chi = 0$) in order to simplify the discussion. In the expressions (20′) and (20″), all quantities of the form $\exp[\pm iD_i(t' \pm \tau)]$ have now to be replaced via

$$\exp[\pm iD_i(t' \pm \tau)] \rightarrow \exp\left\{\pm i\left[\left(\int_\tau^{\tau+t'} \pm \int_0^{\tau}\right) D_i(t)\, dt\right]\right\}. \tag{38}$$

The first term of $\mathcal{S}_i(t')$ in (20′), which was completely focussed at time $t' = \tau$, then has

an amplitude $\mathcal{A}(\tau)$ given by

$$\mathcal{A}(\tau) = -\frac{e^{2i\varphi}\sin^2\psi}{2} \subset \mathrm{Re}\left\langle \exp\left\{+i\left[\left(\int_\tau^{2\tau} - \int_0^\tau\right) D_i(t)\,dt\right]\right\}\right\rangle \supset \qquad (39)$$

where the brackets $\langle \ldots \rangle$ represent an average on the random function $D_i(t)$. The damping factor of $A(\tau)$ is correctly given by the theory developed in § 4 only when the linewidth originating in the intramolecular interactions overcomes the contribution of the intermolecular interactions. In this case, the term $A(\tau) = \mathcal{A}(\tau)$. $\mathcal{F}_+(\tau)$ is easily deduced from the signals $S(\tau)$ obtained for ($\psi = \pi/2$, $\varphi = 0$) and ($\psi = \pi/2$, $\varphi = \pi/2$). It is however possible to observe $A(\tau)$ with a damping factor $\mathcal{F}_+$ close to unity if the angle ψ is chosen small enough. $A(\tau)$ corresponds then to the broken curve in figure 6 (in the absence of motion). One can in this way follow the statistical average on the different molecules of the expression (39) up to times $T_2^* = 2\tau$ which can be an order of magnitude greater than the conventional transverse relaxation time T_2. Different physical models for the motion may then be considered to fit the experimental form of $A(\tau)$. This method would be of value in the investigation of the glass transition found in ortho–para-H_2 (or D_2) alloys, for which the lineshape and FID studies have left open questions concerning the behaviour of the orientational states at the transition (Sullivan *et al* 1978, 1982). This intriguing problem is attacked in paper II using another NMR method especially adapted to the investigation of the glassy phase.

7. Conclusion

We have developed a theory of solid echoes in spin-1 systems under the assumption of the quenching of the flip-flop transitions induced by the dipolar interactions between the spins. Similar calculations may be carried out for other systems when this condition is fulfilled, but this would lead to more complicated results as the complexity of the spin system is raised. In solid $^{15}N_2$ and in solid H_2 this theory is in good agreement with all experimental data reported. The fact that the damping of the solid echo vanishes as the rotation angle ψ tends to zero suggests interesting prospects for the study of rotational motion in molecular solids and provides the possibility of exploring a regime of slow motion for which the NMR lineshapes are quite insensitive.

Acknowledgments

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NMR pulse studies of molecular solids: $^{15}N_2$ and H_2: II. Stimulated echoes and slow rotational motions

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Abstract. Following a description of the formation of stimulated echoes in orientationally ordered crystals such as solid N_2 and solid H_2 we discuss the exploitation of these echoes for the detection of slow rotational motions in these systems. For solid N_2 at low temperatures where the molecular orientations remain fixed the 'natural' decay of the echoes is very slow as a result of the quenching of the nuclear spin flip-flop transitions between different molecules. The 'natural' decay is also very slow in the orientationally ordered phases of solid H_2 and we have used this property to search for residual rotational motion in the quadrupolar glass phase of solid H_2. Such motion would lead to a strong additional damping of the stimulated echoes. The experimental results show that the molecular orientations in the glass phase of H_2 are frozen for time scales up to 10^{-2} s. The temperature dependence of the echo amplitudes in the glass transition region clearly indicates a collective freezing of the molecular orientations. A new model of an inhomogeneous dynamical freezing is proposed to account for the experimental results.

1. Introduction

This is the second paper of a series devoted to the use of NMR pulse techniques for studying orientational ordering in molecular solids and in particular solid nitrogen and solid hydrogen. As discussed in the preceding paper (Estève and Sullivan 1982; hereafter referred to as paper I) the interest in these systems lies in the great variety of orientationally ordered phases obtained at low temperatures. This ordering of the molecular orientations results from the anisotropic interactions between the molecules. For the simplest molecular solids, solid hydrogen and solid nitrogen, the transitions to the ordered phases are driven by the interactions between the quadrupole-bearing molecules, ortho-hydrogen and nitrogen (para-hydrogen molecules are in a spherically symmetric state and do not participate in the ordering).

One of the most fascinating problems encountered in the molecular solids is the existence of glass-like phases in which the molecular orientations become frozen without any significant periodic correlation from one site to another throughout the crystal. The properties of these phases are not fully understood at present and in this paper we discuss the development of a new NMR technique designed specifically to probe the properties of these glasses.

The most striking example of the orientational glasses is probably that observed in the solid hydrogens when the quadrupole-bearing molecules are replaced by a sufficient number of inert diluants. Analogous phases are expected for solid mixtures of nitrogen and argon.

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Whereas in pure systems the ortho-hydrogen and nitrogen molecules adopt long-range-ordered configurations (a Pa_3 structure consisting of four interpenetrating simple cubic sublattices) (see Silvera 1980 for a general review), a new type of orientational ordering has been recognised for ortho–para hydrogen alloys having ortho concentrations $X < 58\%$. In these alloys the orientational degrees of freedom appear to be randomly frozen. This has been deduced from numerous NMR lineshape and free induction decay (FID) studies (Husa and Daunt 1978, Sullivan *et al* 1978, 1979, Cochran *et al* 1980, Washburn *et al* 1980). The physical origin of this new phase, which we have called a quadrupolar glass phase (Sullivan *et al* 1978), is intimately related to the frustration (Toulouse 1977) and the substitutional disorder in the solid mixtures and is believed to belong to the general class of the spin-glass problem. In order to understand the problem of frustration and the effect of disorder in these systems we must consider the constraints imposed on the possible orientational configurations by the topology of the lattice structure. For an isolated pair of electric quadrupoles the lowest-energy configuration is that for which the molecules are mutually perpendicular (a T shape). For a pure system it is immediately obvious that it is impossible in a 3D lattice to arrange all the molecules so that they are mutually perpendicular. A compromise is reached and for pure systems the molecules orient according to the Pa_3 structure (referred to above) (the transition is accompanied by a lattice transformation from the high-temperature HCP structure to an FCC lattice).

If the quadrupoles in this frustrated system are replaced by 'inert' molecules (e.g. para-hydrogen) the substitutional disorder so created has important consequences that do not occur in the absence of frustration. It leads to large reorientations of the quadrupole-bearing molecules in the neighbourhood of the inactive diluants and the disappearance of long-range order when the quadrupole concentration is reduced below 55%. Below this critical concentration the nature of the orientational ordering is profoundly modified. The HCP lattice is apparently stable down to very low temperatures (Gates *et al* 1979) and the NMR experiments indicate that the molecular orientations vary in a random fashion from one site to another—both the directions of the local equilibrium axes and the degree of orientation with respect to these axes vary randomly throughout a given crystal. (The precise specification of the orientational degrees of freedom is given in paper I.)

The orientational ordering in these systems raises important questions concerning the time scale for which we can affirm that the molecular orientations are really fixed. Conventional continuous-wave (CW) and free-induction-decay (FID) NMR techniques have only been able to show that the orientational degrees of freedom appear to be fixed for times up to 10^{-4}–10^{-5} s. A considerable improvement may be achieved by the analysis of solid echoes (as discussed in paper I) for which the observation times during which one can follow molecular reorientations are extended to an effective relaxation time T_2^* (see paper I) which may (by a suitable choice of pulses) be much longer than the transverse relaxation time T_2 that limits the conventional techniques.

The important questions that we address in this paper are:

(i) whether or not the freezing of the molecular motion persists for time scales much longer than those previously established for the glass phase, and

(ii) how the freezing occurs on cooling through the transition region.

In order to answer these questions a new type of experiment capable of following the molecular reorientations for observation times much longer than those relevant for the CW and FID studies was clearly needed.

Stimulated echoes (hereafter abbreviated to StE to avoid confusion with SE which is often used in the literature to designate solid echoes) are particularly well adapted to this problem. They have been applied to the measurement of spin-diffusion constants (Tanner 1970) and more recently to the study of infrequent jumps of complex molecules such as hexamethylene tetramine (Lausch and Spiess 1980, Spiess 1980). We have developed the method StE to study the dynamics in molecular solids that can present orientationally ordered phases at low temperatures. We shall show here how StE following the pulse sequence ($\pi/2$–τ–$\pi/2$–t_W–$\pi/2$) can be used to study the molecular motion in solid nitrogen and solid hydrogen. This relies on two facts:

(i) the 'natural' decay time (for a rigid lattice) of the StE (relative to t_W) is very much longer than T_2; and

(ii) the StE are strongly damped by any variation of the molecular orientational parameters during the waiting time t_W.

We now discuss these points in detail.

A formal treatment of the formation of StE in solid N_2 and solid H_2 is given in § 2 and the natural decay of the StE observed in solid N_2 at low temperatures when the molecular orientations remain fixed is discussed in § 3. After presenting the experimental results for the natural decay for fixed molecules we then describe in § 4 the expected decay of the StE in the presence of molecular motion. This is used in § 5 to discuss the implications of the observed decay for the motion in the quadrupolar glass phase of solid H_2.

2. Formation of stimulated echoes in solid hydrogen and solid nitrogen ($^{15}N_2$)

We consider in this section an assembly of H_2 or $^{15}N_2$ molecules ($I_{\text{total}} = 1$) in well defined orientational states (see § 2 of paper I). In a first approximation we will treat the system as a set of independent molecules and then later on consider the effect of intermolecular nuclear spin–spin interactions. The nuclear spin Hamiltonian in the rotating frame is then limited in this approximation to the secular part of the intramolecular nuclear interactions

$$H^0 = -\hbar \sum_i D_i(\tfrac{2}{3})^{1/2}(3I_{Z_i}^2 - 2)/6^{1/2} + \chi_i I_{Z_i} \tag{1}$$

with $D_i = Dp_i(3\cos^2\theta_i - 1)/2$ and $\chi_i = \chi p_i(3\cos^2\theta_i - 1)/2$. D is the intramolecular dipole–dipole interaction constant and χ the asymmetric chemical shift ($\chi = 0$ for H_2). θ_i is the angle between the motional symmetry axis $\hat{\zeta}$ and the external magnetic field. p_i is the orientational order parameter discussed in the preceding paper. We denote by $\mathcal{D}_i$ the quantity Dp_i in the following.

The formation of the StE following the pulse sequence of figure 1 can now be understood as follows. The first preparatory pulse creates a transverse magnetisation in the rotating frame. Under the influence of the Hamiltonian given by equation (1), which contains both linear and bilinear terms, the evolution during the short time $\tau(\ll T_2)$ leads to the formation of nuclear spin states described by a density matrix operator $\rho(\tau)$ which contains terms linear and bilinear in the nuclear spin variables. The transverse components of $\rho(\tau)$ are transferred by a second pulse $R(\psi)$ into longitudinal components corresponding to spin polarisation and spin alignment. These quasi-invariants are now 'stored' during a waiting period t_W (chosen short compared with the longitudinal relaxation times). The transverse components which remain after the second pulse die away

on a time scale of the order of T_2. After the waiting period $t_W \gg T_2$ the stored components can now be 'read' by means of a third pulse of rotation angle ψ'. The spin polarisation and spin alignment 'stored' during t_W are transferred by the third pulse into coherent transverse states, which then evolve in a reverse manner to that occurring during the first evolutionary period τ and an echo is formed after a delay time τ following the third pulse. The essential point is that the evolution *after* the waiting time t_W is determined by the values of the molecular parameters $p_i(t_W)$ and $\theta_i(t_W)$ which determine H^0 at times t_W. Any evolution of these parameters during $t_W(\gg T_2)$ impairs the focussing of the echo and the motion can be followed by studying the variation of the StE amplitude as a function of t_W.

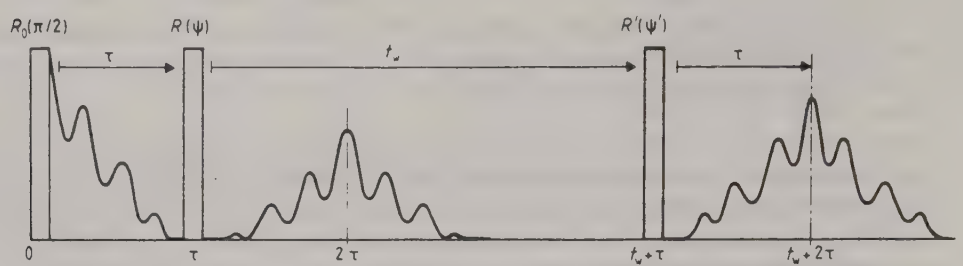

Figure 1. RF pulse sequence for the formation of a stimulated echo. After a preparatory $\pi/2$ pulse, the transverse nuclear spin states (both linear and bilinear) created during τ are transferred by the pulse R to corresponding spin polarisations and spin alignments. These invariants stored during t_W are reconverted by the reading pulse R' to transverse nuclear states which evolve in a manner similar to that during the first period τ and thus focus to give an echo a time τ after R'. When the time t_w is not too long compared with the transverse relaxation time T_2 one can also observe additional echoes.

The formalism developed in paper I for solid H_2 and solid $^{15}N_2$ can now be used to calculate the dependence of the echo amplitude on the molecular parameters and the pulse lengths. We have shown in paper I that the invariant components of the density matrix following a $(\pi/2\text{–}\tau\text{–}\psi)$ sequence for the evolution Hamiltonian of equation (1) are given by

$$\rho_i = \alpha_i \omega_0 I_{z_i} + \beta_i D_i (\tfrac{2}{3})^{1/2} I^2_{i0} \tag{2}$$

with

$$\alpha_i = -(1/\omega_0)(\cos D_i\tau \cos \chi_i\tau) \sin \psi$$

and

$$\beta_i = -6^{1/2}(1/(\tfrac{2}{3})^{1/2} D_i)(\sin D_i\tau \sin \chi_i\tau)(\sin 2\psi)/2. \tag{2'}$$

The normalised second-rank tensor

$$I^2_{i0} = (3I^2_{z_i} - 2)/6^{1/2}$$

is the spin-alignment operator.

After the waiting period t_W the third pulse transforms the invariant components of $\rho(\tau)$ given by (2) into transverse states whose subsequent evolution can be calculated in the same manner as that used to obtain equation (2). As far as the signal detected in the

NMR coil is concerned we are only interested in the transverse vectorial components occurring a time t'' after the third pulse. Using the results of paper I one can show straightforwardly that these components are given by

$$\rho_i'(t'') = \alpha_i\omega_0 \sin\psi' \cos D_i t''(I_{x_i}\cos\chi_i t'' - I_{y_i}\sin\chi_i t'')$$
$$+ \tfrac{1}{2}\beta_i D_i \sin 2\psi' \sin D_i t''(I_{x_i}\sin\chi_i t'' + I_{y_i}\cos\chi_i t''). \tag{3}$$

(For the moment we consider the molecular parameters D_i, χ_i as remaining fixed during the sequence.)

A convenient interpretation of equation (3) is to recognise $\alpha_i\omega_0$ and β_i as the ratios of the inverse Zeeman and intramolecular dipolar spin temperatures to the initial inverse Zeeman temperature (T^{-1}_{crystal}) before the pulse sequence. The transverse magnetisation detected along the x axis by the NMR coil is then

$$M_x = (\mathrm{Tr}\,\rho_i'(t'')I_{x_i}/\mathrm{Tr}\,I_{x_i}^2) = \subset\alpha_i\omega_0 \sin\psi' \cos(D_i t'')\cos(\chi_i t'')\supset$$
$$+ \subset\tfrac{1}{2}\beta_i D_i \sin 2\psi' \sin(D_i t'')\sin(\chi_i t'')\supset \tag{4}$$

where following the notation of paper I the symbols $\subset\ldots\supset$ denote a statistical average over different molecules. Using the values of α and β calculated above this can be written in a form that demonstrates the focussing of the stimulated echo at $t'' = \tau$

$$M_x = -\tfrac{1}{4}\sin\psi\sin\psi' \subset[\cos D_i(t''-\tau) + \cos D_i(t''+\tau)][\cos\chi_i(t''-\tau)$$
$$+ \cos\chi_i(t''+\tau)]\supset - \tfrac{3}{16}\sin 2\psi \sin 2\psi' \subset[\cos D_i(t''-\tau) \tag{5}$$
$$- \cos D_i(t''+\tau)][\cos\chi_i(t''-\tau) - \cos\chi_i(t''+\tau)]\supset.$$

Let us now introduce the weak intermolecular nuclear dipolar Hamiltonian $H_d = H_d' + H_d''$; H_d' and H_d'' being respectively the secular and non-secular parts of H_d with respect to H^0. We shall suppose that neighbouring molecules are in different orientational states so that their NMR frequencies differ by an amount $\sim D$ (the scale of the fine structure due to the intramolecular interaction $H^{\text{sec}}_{\text{intra}}$) which is much greater than the strength d of H_d. In this situation we have seen in the preceding paper that the flip-flop transitions induced by H_d'' are almost completely quenched, at least on a time scale of the order of d^{-1}. We shall consider the case when the preparation time τ is sufficiently short that the density matrix ρ_i just after the second pulse is correctly given by expression (2) above. If there is a wide distribution of orientational states, the conditions $\subset D_i^2\supset^{1/2}\tau \gg 1$ and (for solid N_2) $\subset\chi_i^2\supset^{1/2}\tau \gg 1$ are both fulfilled, the amplitude of the StE is maximum at $t'' = \tau$ and has the value

$$A(\tau, t_W) = -\tfrac{1}{4}\sin\psi\sin\psi'(1 + 3\cos\psi\cos\psi') \qquad \text{for solid } {}^{15}N_2 \tag{6}$$

or

$$A(\tau, t_W) = -\tfrac{1}{2}\sin\psi\sin\psi' \qquad \text{for solid } H_2. \tag{6'}$$

In terms of α and β, these amplitudes may be written in the more meaningful form

$$A(\tau, t_W) = -\sin\psi\sin\psi'\,(\subset\alpha_i^2\supset\omega_0^2 + \tfrac{1}{3}\subset\beta_i^2 D_i^2\supset\cos\psi\cos\psi') \qquad \text{for solid } {}^{15}N_2 \tag{7}$$

or

$$A(\tau, t_W) = -\sin\psi\sin\psi' \subset\alpha_i^2\supset\omega_0^2 \qquad \text{for solid } H_2. \tag{7'}$$

The density matrix $\rho_i(\tau)$ after the second pulse (expression (2) above) is invariant with respect to the Hamiltonian $H^{sec}_{intra} + H'_d$. The transitions induced by H''_d can *only* restore equilibrium between the Zeeman temperature α_i and the dipolar temperature β_i. Since these transitions are almost completely quenched this approach to equilibrium is very slow. In order to simplify the discussion we consider the particular case $\psi = \pi/2$ for which the density matrix ρ_i is purely vectorial ($\beta_i = 0$). If the Zeeman temperatures change during the waiting time t_W, the relations (7) are simply replaced for $\psi' = \pi/2$ by

$$A(\tau, t_W) = \lambda \subset \alpha_i(0)\alpha_i(t_W) \supset \tag{8}$$

with $\lambda = -\omega_0^2$ for solid $^{15}N_2$ and $\lambda = -2\omega_0^2$ for solid H_2. During the relaxation process (due to H''_d) only the average $\subset \alpha_i \supset$ remains constant and the stimulated echo decays from $A^0(\tau, t_W = 0) = \subset \alpha_i^2(0) \supset$ to the value $\subset \alpha_i(0) \supset^2$ which can *only* be smaller than $\subset \alpha_i^2(0) \supset$.

When the effect of H_d must be taken into account during the preparation time τ, the expression (2) is only approximate. Once again if we separate H_d into secular and non-secular parts, H'_d and H''_d respectively, we observe that there are invariants if we neglect H''_d. These invariants are the average values of the spin polarisation $\langle I_{z_i} \rangle$ and spin alignment $\langle I_{i0}^2 \rangle$ which would still be conserved for each molecule during the waiting time t_W. The StE amplitudes would be constant as soon as $t_W > d^{-1}$. (This can be shown by a more detailed analysis of the true evolution of the density matrix.) The decay of the StE is therefore clearly linked to the flip-flop transitions induced by H''_d. Their quenching, which is known to occur also in the presence of the strong magnetic field gradients that surround paramagnetic impurities in solids or vortices in type II superconductors, has been called dynamical quenching (Genack 1976).

3. Natural decay of stimulated echoes in orientationally ordered solid nitrogen

We have studied the decay of StE in polycrystalline samples of solid $^{15}N_2$ at 4.2 K for which the molecular orientations remain fixed.

In the Pa_3 structure adopted by the molecules at low temperatures ($T < 36$ K), two nearest-neighbour molecules are aligned along different directions (their angular separation is $\cos^{-1}(\frac{1}{3})$) and as a result, in most crystals†, the NMR frequencies (determined by the eigenvalues of H^{sec}_{intra}) will differ by values ($\sim D$) much larger than the strength d of the intermolecular interactions and flip-flop transitions (induced by H''_d) are severely quenched. The next-nearest-neighbour molecules in the Pa_3 structure are however parallel, their NMR frequencies are identical and flip-flop transitions are partially allowed between their spins as discussed in paper I. These transitions will however play no role in the damping of the echoes since these molecules are prepared with the same Zeeman and dipolar temperatures.

The observed StE amplitudes following a ($\pi/2$–τ–$\pi/2$–t_W–$\pi/2$) sequence are reported in figure 2 for two values of τ. The decay of the echoes with the waiting time t_W shows the same behaviour for different preparation times τ. The amplitudes first decrease logarithmically with time until the decay is almost complete at t_W^c for which

$$A(\tau, t_W^c) \simeq 0.1A(\tau, t_W = \tau).$$

† The NMR frequencies also depend on the orientation of the external field with respect to the alignment of the molecules and the NMR frequencies will coincide only for a negligible number of crystals in the powder specimens.

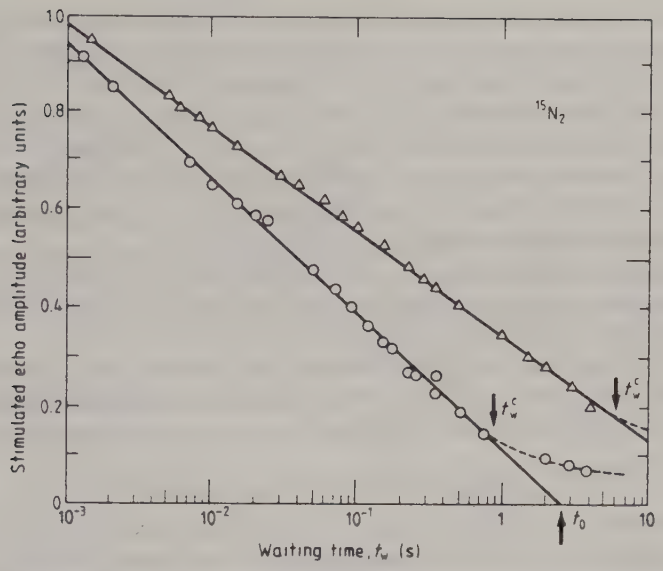

Figure 2. The natural decay of the ($\pi/2$–τ–$\pi/2$–t_W–$\pi/2$) stimulated echo in solid $^{15}N_2$ at 4 K for which the molecular orientations remain fixed. This pulse sequence stores spin polarisations only during T_W. The unusual logarithmic decay for $0 < t_W < t_w^c$ crosses over to a slower decay regime for $t_W > t_w^c$. Triangles: $\tau = 2$ ms; circles: $\tau = 4.4$ ms.

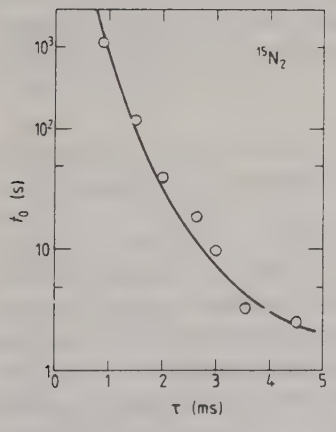

Figure 3. Dependence of the characteristic time scale t_0 of the natural decay (figure 2) as a function of the preparation period τ.

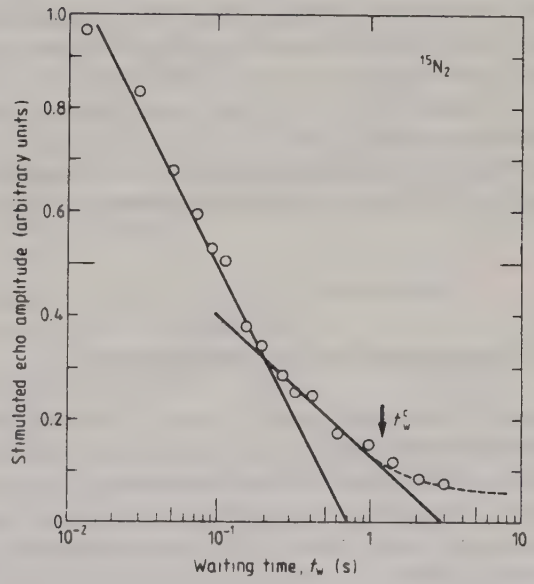

Figure 4. The natural decay of the ($\pi/2$–τ–$\pi/4$–t_W–$\pi/4$) stimulated echo in solid $^{15}N_2$ at 4 K. This sequence stores spin alignment as well as spin polarisation during t_W. The logarithmic decay of figure 2 is now separated into two parts related to the different equilibration rates of the Zeeman and dipolar temperatures.

For times $t_W > t_W^*$ one then observes a crossover to a different decay regime for which the decay rate is much slower. We have not investigated this second regime in detail since the times become comparable to the measured longitudinal relaxation times for our samples and the amplitudes were very small. If the first regime continued uninterrupted, the StE amplitude would fall to zero at a time t_0. This time, as shown in figure 3, decreases on increasing the preparation time τ. For all the experiments reported here we estimate (see below) that the homogenisation of the Zeeman temperatures was *not* achieved for times t_W^* characterising the regime crossover.

As expected, the StE decay is much slower than the decay of the solid echoes discussed in paper I. More unexpectedly, the observed logarithmic time dependence is rather unusual for a relaxation process and remains unexplained.

We have also studied the StE following a $(\pi/2\text{–}\tau\text{–}\pi/4\text{–}t_W\text{–}\pi/4)$ sequence in order to compare the homogenisation rates of the Zeeman and dipolar temperatures. The amplitude of the StE decay following this sequence may be written in the form

$$A(\tau, t_W) = -\tfrac{1}{2} \subset \alpha_i(0)\alpha_i(t_W) \supset \omega_0^2 - \tfrac{1}{12} \subset \beta_i(0)\beta_i(t_W) D_i^2 \supset. \tag{9}$$

The time dependence of the StE decay for this sequence is shown in figure 4. The logarithmic regime $0 < t_W < t_0$ discussed above is now divided into two parts. This may be understood if the dipolar temperatures return to thermal equilibrium faster than the Zeeman temperatures but once again with a logarithmic decay characterised by a shorter critical time t_0.

All these results clearly show that the dynamical quenching of the flip-flop transitions is effective in solid N_2, but also that the StE decay is far from simple and not characterised by a single exponential relaxation rate. Experiments on single crystals for which the NMR frequencies and thus the quenching conditions are both known and variable (by changing the field direction) should provide more insight into the decay process and tell us whether the logarithmic behaviour is significant or merely the result of the superposition of many exponential decays with a wide distribution of relaxation rates.

Despite the lack of a precise quantitative description of the natural decay of the StE, the experimental results for the case of rigid molecular orientations (solid N_2 at 4 K) provide an important step in our use of the StE to detect the presence of molecular motion. This theme is developed in detail in the next section.

4. The motional decay of stimulated echoes

In addition to the natural decay of the stimulated echoes discussed above for rigid molecular orientations, the echo emplitudes will *also* be damped by any molecular motion. We consider firstly the case of very slow rotational motions for which the orientations may be considered fixed during the short preparation time τ, but not necessarily during the much longer waiting time t_W. In this case the nuclear spin evolution from the time $t_W + \tau$ to $t_W + 2\tau$ no longer compensates the evolution between 0 and τ and the StE is partially destroyed. In order to simplify the discussion we consider only isolated ortho-hydrogen molecules that have fixed intrinsic order parameters (see paper I) but whose orientations given by the angles θ_i between the symmetry axes $\hat{\zeta}_i$ and the applied magnetic field are allowed to change during the time t_W. As a result of this motion the StE amplitude following a $(\pi/2\text{–}\tau\text{–}\pi/2\text{–}t_W\text{–}\pi/2)$ is no longer given by the value

$-\frac{1}{2}$ but by the average

$$A(\tau, t_w) = -\subset\cos(D_i(0)\tau)\cos(D_i(t_w)\tau)\supset$$
$$= -\tfrac{1}{2}R_e\subset\exp(i(D_i(t_w) - D_i(0))\tau)\supset$$
$$= -\tfrac{1}{2}R_e\subset\exp[i\mathfrak{D}_i\tau(P_2(\theta(t_w)) - P_2(\theta(0)))]\supset. \quad (10)$$

(The $P_2(\theta)$ are the conventional Legendre polynomials.)

We shall suppose that the motion is a random process and that a distribution function $\mathbb{P}(\gamma, t_w)$ can be used to describe the probability that the symmetry axis rotates by an angle γ during the time t_w. Using the addition theorem for the spherical harmonics, one deduces

$$\Delta P_2(\theta_i, t_w) = P_2(\theta_i(t_w)) - P_2(\theta_i(0))$$
$$= -\tfrac{3}{2}\sin^2\gamma(3\cos^2\theta_i(0) - 1)/2$$
$$-\tfrac{3}{4}\sin 2\theta_i(0)\sin 2\gamma\cos(\varphi - \alpha) + \tfrac{3}{8}\sin^2\theta_i(0)\sin^2\gamma\cos 2(\varphi - \alpha). \quad (11)$$

The angles are defined in figure 5.

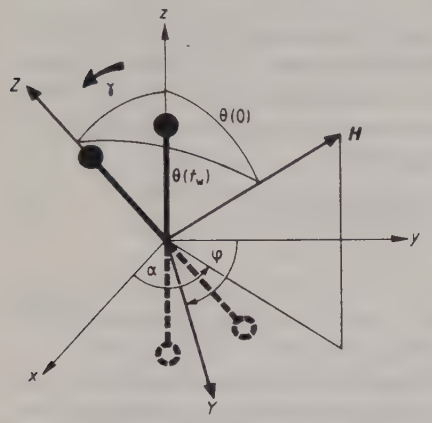

Figure 5. Definition of the angles specifying the molecular orientations.

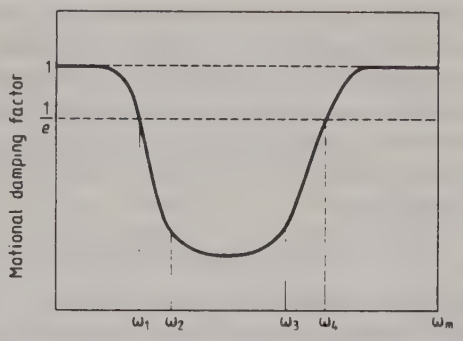

Figure 6. Schematic representation of the expected variation of the stimulated echo amplitude as the motional frequency ω_m increases.

The motional damping factor $a(\tau, t_w)$ for the StE is therefore linked to the probability density $\mathbb{P}(\gamma)$, assumed to be the same for all molecules, by the relation

$$a(\tau, t_w) = \mathrm{Re}\left(\int \exp(i\mathfrak{D}_i\tau\Delta P_2(\theta_i))\mathbb{P}(\gamma, t_w)\frac{\sin\gamma\,d\gamma\,d\alpha\,d\varphi\sin\theta\,d\theta}{2\pi}\right). \quad (12)$$

Even if the detailed form of $\mathbb{P}(\gamma, t_w)$ is not known, it is nevertheless possible to estimate the decay factor $a(\tau, t_w)$ by replacing the probability distribution of the quantity $u = \mathfrak{D}_i\tau\Delta P_2(\theta, t_w)$ by a Gaussian distribution related to the mean square deviation of u. Within this approximation, the average (12) is readily performed:

$$a(\tau, t_w) = \int \exp(iu)\mathbb{P}(u)\,du \simeq \exp(-\tfrac{1}{2}\subset u^2\supset). \quad (13)$$

The mean square $\subset u^2\supset$ calculated using expression (11) is given by

$$\subset u^2\supset = \subset\mathfrak{D}_i\tau\supset^2(0.6\langle\sin^2\gamma\rangle - 0.1125\langle\sin^4\gamma\rangle). \quad (14)$$

(We recall that the average $\langle\sin^2\gamma\rangle$ is taken over the molecular motion.)

If furthermore the second term in (14) may be neglected, one obtains the following estimation for the motional decay factor:

$$a(\tau, t_W) \simeq \exp(-0.3 \subset \mathcal{D}_i^2 \supset \tau^2 \langle \sin^2 \gamma(t_W) \rangle). \tag{15}$$

This formula clearly shows that very small rotations are indeed detectable since the StE may be observable with a factor $\subset \mathcal{D}_i^2 \supset \tau^2$ much larger than unity.

The absolute resolution is limited in two ways:

(i) τ may not be much greater than T_2; and

(ii) the waiting time t_W is limited by the natural decay of the StE for a given τ.

We now discuss how the behaviour of the StE varies with the characteristic frequency ω_m of the rotational motion. We consider the case where the motion can be described by a single correlation time $\tau_m = \omega_m^{-1}$ which increases continuously (e.g. as a function of the temperature) from 0 to values greater than D. (The former correspond to the motional narrowing regime (Abragam 1961).)

We can for this simplification write the average of $\sin^2\gamma(t_W)$ as

$$\langle \sin^2 \gamma(t_W) \rangle \simeq \tfrac{2}{3}(1 - e^{-t_W/\tau_m}). \tag{16}$$

It then follows from the above discussion that the motional damping starts to become effective when $\omega_m \geqslant \omega_1 = 5\,(\subset \mathcal{D}_i^2 \supset \tau^2 t_W)^{-1}$ (we assume here that $\subset \mathcal{D}_i^2 \supset \tau^2 \gg 1$). When the motional frequency ω_m reaches the value $\omega_2 = t_W^{-1}$, the evolutions during the preparation period ($0 < t < \tau$) and the detection period ($t_W + \tau < t < t_W + 2\tau$) becomes completely uncorrelated, and the average (10) is simply given by

$$a(\tau, t_W) = [\langle \exp(i\mathcal{D}_i \tau P_2(\theta_i(0))) \rangle \langle \exp(i\mathcal{D}_i \tau P_2(\theta_i(t_W))) \rangle] \tag{17}$$

which reduces to

$$a(\tau, t_w) = |\langle \exp(i\mathcal{D}_i \tau P_2(\theta_i)) \rangle|^2. \tag{18}$$

The StE is thus almost completely destroyed since $\subset \mathcal{D}_i^2 \supset \tau^2 \gg 1$.

When the motional angular frequency ω_m is very high the evolution of the molecular parameters during the time τ (in both the preparation and detection periods) can no longer be neglected†. The expression (14) must now be replaced in a straightforward way by the correct one

$$a(\tau, t_W) = \subset |\langle \exp(i\mathcal{D}_i \int_0^\tau P_2(\theta_i(t))\, dt) \rangle|^2 \supset. \tag{19}$$

When complete motional narrowing occurs during the time intervals τ, $P_2(\theta(t))$ averages to zero, and the StE recovers its initial value (i.e. the value in the absence of any motion). This restoration of the StE sets in when the motional frequency reaches the value $\omega_3 = (D\tau^2)^{-1}$ and is complete for $\omega_m \geqslant \omega_4 = D^2\tau$. (This is easily found from the conventional theories of motional narrowing as described for example by Abragam 1961.)

The whole evolution of the StE amplitudes as the molecular motion increases is sketched in figure 6. The motional damping is effective for the frequency range $\omega_1 < \omega_m < \omega_4$ with $\omega_4/\omega_1 = (D^2\tau^2)^2 t_W/\tau$.

† It should be noted that as a result of small crystal-field interactions and local orientational correlations small but non-vanishing order parameters exist even in the orientationally disordered phases and the values of these parameters ($0.01 < \sigma < 0.1$) are sufficient to ensure that the free induction signal following the first pulse has decayed before the application of the second pulse.

For the physical problem discussed in this paper (and analysed in detail in the following sections) this frequency range for which it is possible to observe the molecular motion can for practically realisable cases extend over several decades.

In solid N_2, the above theory is complicated by the presence of the anisotropic chemical shift but the general results still hold with slight modifications. Using the results of § 3, we estimate that the lowest detectable motional frequency for solid $^{15}N_2$ is less than 10^{-2} rad s^{-1}.

5. Stimulated echoes in the quadrupolar glass phase of solid hydrogen

The quadrupolar glass phase discussed briefly in the introduction has been observed in solid ortho–para-hydrogen alloys for ortho-hydrogen concentrations $0.15 < x < 0.58$ (Sullivan *et al* 1978) and in para–ortho-deuterium alloys for para-deuterium concentrations $x < 0.56$ (Sullivan *et al* 1979). (In the case of deuterium it is the para-molecules that possess electrostatic quadrupole moments while the ortho-species are spherically symmetric). In both cases the low-temperature NMR spectra have a bell shape flanked by well defined shoulders. These lineshapes are directly related to the orientational order parameters (Sullivan *et al* 1978) and at least for time scales $t < d^{-1}$ ($\sim 10^{-5}$ s in both cases) one draws the inference that the orientational degrees of freedom are frozen in a random fashion throughout the sample. It should be recalled here that ortho-H_2 and para-H_2 molecules are quantum mechanical rotators (orbital angular momentum $J = 1$) and the orientational degrees of freedom include both the local symmetry axes specifying the alignment of the molecules *and* the intrinsic purely quandrupolar order parameters $\sigma_i = \langle 3J_{z_i}^2 - 2\rangle_Q$ and $\eta_i = \langle J_{x_i}^2 - J_{y_i}^2\rangle_Q$ (we use the notation $\langle\ \rangle_Q$ to emphasise the fact that the brackets refer to a quantum mechanical average). The NMR results for both powder specimens (Sullivan *et al* 1978) *and* single crystals (Washburn *et al* 1980) show that the alignment remains axially symmetric $\eta_i \simeq 0$ and that there is a broad distribution for the remaining order parameters. For the quantum mechanical rotators the p_i of equation (1) are given by $p_i = \frac{2}{3}\sigma_i$ in the manifold $J = 1$.

As the samples are warmed the characteristic lineshapes of the quadrupolar glass are maintained up to a critical temperature region where the wings start to shrink (by approximately 20%) and then disappear in a very narrow temperature interval (e.g. for $x = 0.36$, $T_c = 280 \pm 15$ mK).

Although this rapid variation would alone point to a collective freezing of the quadrupolar degrees of freedom the precise nature of the transition is not clear. The real uncertainties are associated with the question as to whether the transition is a conventional phase transition, and if so what its order is, or whether the transition is attributable to a purely dynamical freezing as believed to be the case for ordinary (window-pane) glasses. This is the central question raised by the spin glasses in general and there is to date no satisfactory answer to this problem.

In view of the importance that detailed information, and in particular any insight into the dynamics near T_c for the quadrupolar glass phase, has for the spin-glass problem in general we have conducted two types of experiments designed to prove the molecular motion for long times $t \gg d^{-1}$.

In the first experiment we measured the decay of stimulated echoes for a sample of ortho-concentration $x = 0.54$ for which the CW lineshape transition occurs at $T_c = 360 \pm 10$ mK. The experimental conditions were chosen to enable us to test for any residual motion for $T \ll T_c$ which would not have been seen for the CW or FID studies.

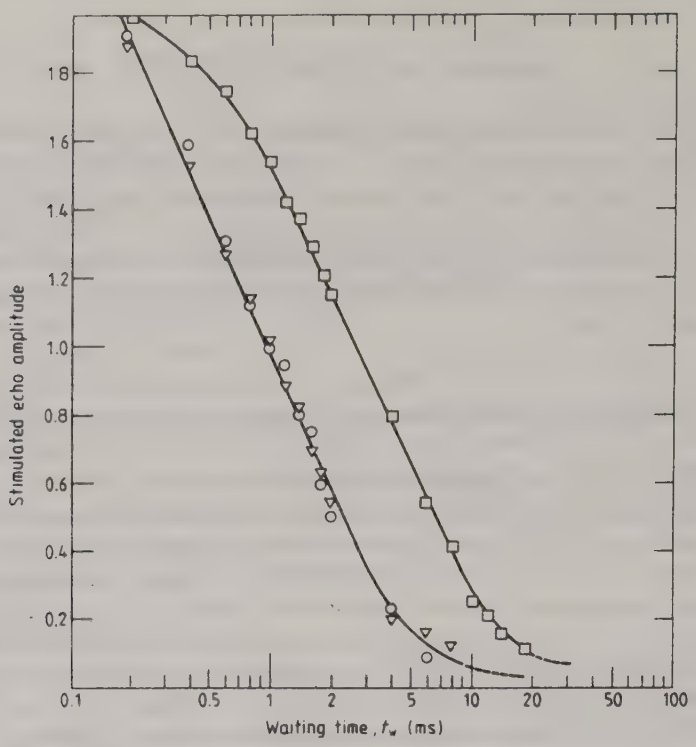

Figure 7. The observed decay of the ($\pi/2$–τ–$\pi/2$–t_W–$\pi/2$) stimulated echo in the quadrupolar glass phase of solid hydrogen (ortho-concentration $x = 0.54$, $T = 220$ mK). The time scale of the logarithmic decay allows us to place severe limits on any residual motion in this phase. Squares: $\tau = 12.5$ μs; circles and triangles: $\tau = 25$ μs.

The decay of the StE observed at 220 mK is shown in figure 7. This decay has the same qualitative behaviour as that observed for solid N_2 and this is probably the natural decay. Unfortunately, in the absence of any reliable theory for the natural decay, we can only use the results to place a lower bound for the time scale of any residual motion. More precisely, using the results of § 4 we estimate

$$\langle \sin^2 \gamma \rangle \leqslant 10^{-1} \qquad \text{for } t_W = 3 \text{ ms}.$$

Since any variation of the order parameters would also damp the StE, a similar inequality may be written for the mean square of their variation during the waiting period t_W. We are therefore led to conclude that the molecular orientational order parameters can be considered frozen for times up to $t_L = 15$ ms using the expression (16). This bound has to be compared with the previous limit of 10^{-5} s for the earlier CW studies. One can note that the reorientational rate in the completely disordered high-temperature phase is typically $\sim 10^{-12}$ s. The orientation of the molecules in the quadrupolar glass phase therefore appears to be really frozen at least to the same extent as the atomic positions in conventional 'window-pane' glasses. We now need to consider the evolution of the freezing of the molecular rotations as one cools through the transition region in order to gain some insight into the nature of this transition, i.e. a conventional phase transition as opposed to a dynamical freezing.

A second type of experiment was conducted for this purpose. This consisted of following the temperature dependence of a given stimulated echo on warming through

the transition region for a sample of 38% ortho-hydrogen. The experimental pulse sequence was chosen so that one could detect a motional damping of the StE for motional frequencies ω_m having values between the limits illustrated in figure 6. For the selected preparation time τ these limits were $\omega_l \simeq 10^5$ rad s^{-1} (assuming that the distribution of the intrinsic order parameters remains constant). The striking result shown in figure 8 is that no really strong damping is ever observed even for temperatures just below $T_c = 290$ mK (the transition temperature for which the shoulders of the NMR lineshapes disappear).

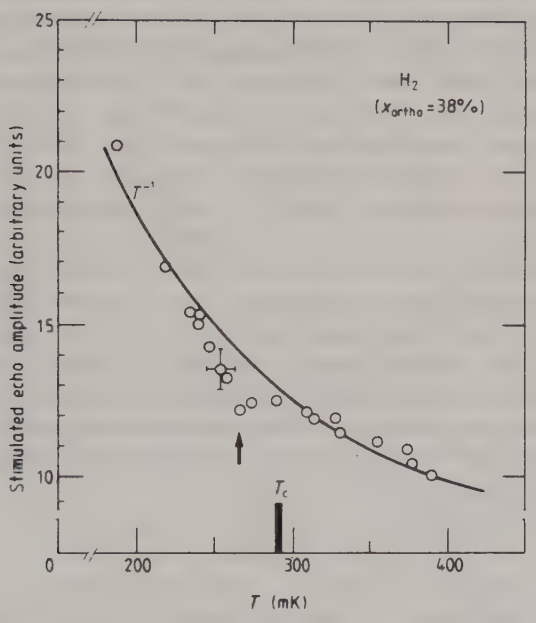

Figure 8. Temperature dependence of the ($\pi/2$–τ–$\pi/2$–t_w–$\pi/2$) stimulated echo in the quadrupolar glass phase of solid hydrogen ($\tau = 25$ μs, $t_w = 2$ ms). These echo amplitudes have been corrected to account for the longitudinal relaxation time T_1. Only a very slight modification of the echo amplitude (indicated by the arrow) is observed on cooling through the glass transition region. T_c (CW) designates the temperature for which one observes changes in the CW lineshapes.

The lack of a significant damping of the StE indicates that no more than 10% of the molecules satisfy the condition for strong damping at a given temperature. This result could be interpreted in two ways: either in terms of an abrupt phase transition (the critical properties: first-order, second-order . . . remaining unresolved within the currently available experimental resolution) or in terms of a dramatic slowing-down of the orientational fluctuations, which are furthermore inhomogeneously distributed throughout the sample—different molecules satisfying the damping condition at different temperatures. Recent spin-lattice relaxation studies (Sullivan and Estève 1981), which have shown a dramatic collapse of the frequency spectrum of the orientational fluctuations on approaching T_c, seem to favour the latter interpretation. The existence of an *inhomogeneous distribution* of the dynamical motion in the sample that one has in this case to invoke for $T \lesssim T_c$ is reminiscent of related properties in RKKY spin glasses.

Temperature inhomogeneities are also present in the hydrogen samples as a result of ortho–para conversion heating, the relatively poor thermal conductivity and the Kapitza boundary resistance between the hydrogen and the copper wires embedded in the samples. The estimated maximum temperature inhomogeneity (of the order of 10 mK) seems to be too small however to explain the effect entirely without also invoking the presence of intrinsic inhomogeneities for the molecular motion below T_c.

We are therefore led to analyse the results in terms of a model of inhomogeneous dynamical freezing which we will discuss at length in a future publication. The features of this model are described as follows. On cooling the crystal in the rotationally disordered phase new structure appears in the lineshape at a temperature T_c signalling that the dynamical motion of some molecules has been slowed down to $\omega_m \leqslant 10^5$ rad s^{-1}. At the same temperature a small motional damping of the StE begins to develop (figure 8), indicating that among these 'slow' molecules only a part of them satisfies the strong-damping condition ($65 < \omega_m < 10^5$ rad s^{-1}). Below T_c, the subsequent slowing-down is clearly inhomogeneous, the evolution of the motion $\omega_m(i)$: $10^5 \rightarrow 65$ rad s^{-1} taking place for each molecule i in a narrow temperature interval δT_m centred at a temperature T_i that has different values at different sites (i.e. in different molecular environments). An estimation of the spread ΔT_i in the T_i can be inferred from (i) the temperature interval for which the CW lineshapes continue to evolve below T_c and (ii) the temperature interval for which a weak motional damping of the StE can be detected. One obtains in this way a spread $\Delta T_i \simeq 50$–80 mK. This spread was found to be the same for several samples having ortho-hydrogen concentrations in the range 35–50%. Since the temperature dependence of the StE amplitudes resulting from the contributions of *all* the molecules show that a fraction $\alpha \simeq 0.1$ of the molecules satisfy the strong-damping condition in the temperature interval $[(T_c - \Delta T_i), T_c]$, one then deduces (assuming a uniform distribution of the T_i) the following estimates for δT_m:

$$\delta T_m \simeq \alpha \Delta T_i$$

which gives $\delta T_m \simeq 5$–8 mK.

In terms of this model there is a dramatic slowing-down of the molecular dynamics by three orders of magnitude for the characteristic frequency in a very narrow temperature interval δT_m. This new picture for the quadrupolar glass transition is described schematically in figure 9. Up to this point, we have proposed a static picture for the distribution of the motional frequencies $\omega_m(i)$. One has to say that it could in its turn have a slow time dependence (leading to an 'exchange' between 'slow' molecules and 'rapid' ones) without requiring that the NMR results be modified. This inhomogeneous dynamical freezing model is clearly consistent with the absence of any anomaly in the specific heat around T_c. Whether or not the system displays a critical behaviour (in a certainly subtle way) during the slowing-down is an important question that we, however cannot answer at the present time.

In any case, an interpretation of the experiments reported here in terms of a non-collective slowing-down of the para-rotational phase seems to be definitely *excluded*. A non-collective behaviour would imply a Boltzmann temperature dependence of the orientational correlation times with activation energies greater than 100 K in order to account for the value of the δT_m. Such energies are completely unrealistic for solid H_2 for which the anisotropic quadrupolar interactions (for a pair of neighbouring ortho-molecules) are of the order 0.8 K*. Another way of looking at the extent to which the freezing is of a collective nature is to calculate the quality factor $Q = \delta \ln \tau (T_c/\delta T)$ for the evolution of the dynamics near T_c. For the δT_m estimated above $Q \geqslant 300$ close to the

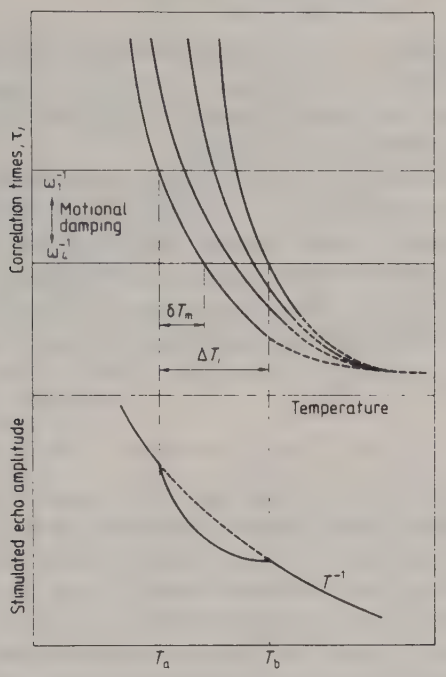

Figure 9. Comparison of the model of an inhomogeneous freezing of the dynamical motion (upper figure) with the temperature dependence of the stimulated echo amplitude (lower figure). In the upper figure each full curve represents the characteristic time τ_i of the molecular motion for different sites. There is a rapid slowing-down in a narrow temperature interval δT_m which occurs at different temperature T_i for different molecules for $T < T_c$. Since the spread ΔT_i is much larger than the δT_m for the range $\omega_4^{-1} < \tau_i < \omega_1^{-1}$ for which *local* contributions to the StE are damped only a weak attenuation of the *total* echo amplitude is observed for $T_a < T < T_b$.

Q-factors of many RKKY spin glasses. One now realises that further experiments are needed to provide information on the dynamics of the molecules on an even finer temperature scale and frequency scale than that reported here in order to gain more insight into the nature of the transition to the glass phases.

This raises serious practical difficulties for solid hydrogen samples which suffer from an intrinsic self-heating due to ortho–para conversion. Although the samples (total volume $\sim 10^{-2}$ cm^3) were grown on a brush of very fine copper wire (0.01 mm) attached to a powerful dilution refrigerator, as pointed out above the Kapitza boundary resistance and the relatively poor thermal conductivity of solid H_2 are such that it seems impossible (using existing techniques) to improve a great deal on the temperature uncertainties quoted above, at least for samples that can be considered as bulk solid rather than thin films. (Thin films would not be expected to be strain free and the collective effects we describe here would be swamped by large crystal-field interactions.) For this reason we are now pursuing similar experiments for deuterium alloys where the conversion rates are much slower and the self-heating much less important than for hydrogen.

Although the results reported here show unambiguously that the molecular rotational motions undergo a collective freezing over a narrow temperature interval we still cannot say whether this is associated with a true phase transition (in the thermodynamic sense) or whether it is the signature of a dynamical gel as is often invoked for the vitreous

transitions of ordinary glasses. Clearer insight into this problem will be possible when more data are available for the solid echoes, stimulated echoes and the longitudinal relaxation rates. The latter are directly related to the power density spectrum of the orientational fluctuations at the Larmor frequency.

This information concerning the dynamics needs to be analysed in conjunction with purely thermodynamic observations: for example, simultaneous measurements of $(\partial P/\partial T)_V$ *and* the heat capacity C_V could tell us if the glass phases were ergodic (in which case $C_V \propto (\partial P/\partial T)_V$ at all temperatures). Experimental evidence for a lack of ergodic behaviour for temperatures below those for which the NMR studies indicate motional freezing would provide strong support for a purely dynamical (i.e. vitreous) transition.

6. Conclusion

The quenching of the flip-flop transitions due to the nuclear spin–spin interactions between different molecules in solid nitrogen and solid hydrogen is very effective and it leads to a very slow natural decay of the stimulated echoes. This allows us to choose waiting times t_W much longer than the decay time (the effective T_2^*) of solid echoes. since the stimulated echoes are also damped by any change in the orientational states during t_W, they can be used to detect very slow molecular motions. Although we have considered only the simplest molecular solids (H_2 and N_2) the technique can, in principle, be used to study the dynamics in more complex systems—the order–disorder transitions in methane, NH_4Cl, deuterated liquid crystals etc—or the vitreous transitions in conventional glasses.

The application of this method to the study of the quadrupolar glass phase of solid hydrogen has allowed us to determine:

(i) that the molecular orientations are truly frozen for times at least longer than 10^{-2} s even just below the transition zone; and

(ii) that there is either an abrupt phase transition (unlikely in view of the absence of any anomaly in the observed thermodynamic properties (Haase *et al* 1980)); or a dramatic slowing-down of the orientational fluctuations in a narrow temperature interval on cooling towards the glass phase. In this last case the important conclusion drawn from stimulated echoes studies is that we must invoke an inhomogeneous distribution for the dynamical motion in the transition regime. Stimulated echoes therefore provide a powerful tool for the study of molecular orientational ordering and the results of experiments on deuterium alloys now being pursued in this laboratory should help us obtain a better understanding of the controversial spin-glass transition.

Acknowledgments

We would like to thank S Leibler and M Richards for numerous fruitful discussions concerning the use of stimulated echoes.

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2) CALCUL DE L'AMORTISSEMENT DES ECHOS STIMULÉS DANS LE CAS D'UN MOUVEMENT BROWNIEN DE ROTATION.

NOTE :

Stimulated echoes damping induced by a rotational diffusion motion.

STIMULATED ECHO DAMPING INDUCED BY A ROTATIONAL DIFFUSION MOTION

D. ESTEVE

Stimulated echoes (St.E.) following a three pulse RF sequence (as shown in figure 1) have been widely used to measure very slow diffusion rates in solids. More recently, it has been shown that they can also be used to detect slow molecular rotational motions[1,2]. These studies of the dynamics in simple molecular solids are especially relevant when these systems display a glassy behavior[2,3]. It is therefore important in order to extract dynamical information from the experiments to know the behavior of St.E. for simple clear-cut models for the molecular motion. For this reason, we have evaluated the motional damping factor of the St.E. for the case of a rotational diffusion motion for axial molecules (such as H_2, N_2, C_2H_2,...).

For this type of molecule, the static part of the secular intramolecular Hamiltonian H_N is proportional to the angular factor :

$$P_2(\Omega) = \frac{3\cos^2\alpha - 1}{2} \qquad (1)$$

where α is the angle between the magnetic field and the axis $\hat{\zeta}$ which is the averaged (over extremely rapid librations) direction Ω of the molecular axis

After two $\pi/2$ pulses separated by a time τ such that $\tau \lesssim d^{-1}$ (where d is the characteristic frequency of the weak intermolecular dipolar interactions), the nuclei of a molecule are prepared in a state of nuclear spin polarisation which depends on the value of the angle α at that time t=0. During the waiting time t_w, the rate at which nuclear spins come back toward thermal equilibrium under the effect of intermolecular dipolar interactions will be very slow if neighbouring molecules have different orientations, since in this case their NMR frequencies will differ by an amount much greater than d. This quenching of the spectral diffusion allows one to observe echoes for waiting times t_w much greater then d^{-1} as discussed in detail in reference [2].

The amplitude of the St.E. focussed at time τ after the third pulse is a sum of terms of the following form[2] :

$$A(\tau, t_w) = \left\langle \cos\left\{ \omega_D \tau \left[P_2(\Omega(t=0)) - P_2(\Omega(t=t_w)) \right] \right\} \right\rangle \quad (2$$

where ω_D is a relevant characteristic NMR frequency related to H_N. If the angles α have changed during t_w, the phase shifts during the preparation and the reading periods are not compensated, and the St.E. is damped. For a molecule containing two dipolar doupled (I=1/2) nuclei (such as H_2), the amplitude of the stimulated echo contains only one term of the form (2) in which ω_D is simply the intramolecular dipolar coupling constant of the molecule[2].

The average involved in (2) has the following meaning :

$$A(\tau,t_w) = \iint \frac{d\Omega}{4\pi}\, d\Omega' P(\Omega\rightarrow\Omega';t) \cos\left\{\omega_D \tau \left[P_2(\Omega) - P_2(\Omega')\right]\right\} \qquad (3)$$

where $P(\Omega\rightarrow\Omega';t_w)$ is the probability that a molecule rotates from the position (Ω) to the position (Ω') during the time t_w.

For a diffusion process, this probability is know in terms of an infinite expansion of Legendre polynomials of the rotation angle[4]. Since this expansion leads to almost intractable calculations, it is worthwhile to develop an approximation somewhat simpler to handle.

At short times, the probability $P(\Omega\rightarrow\Omega';t)$ is essentially distributed in the neighborhood of Ω, and may be evaluated as if the diffusion process occurred in the plane π tangent to the sphere at Ω (see figure 2).

The planar solution of the diffusion equation :

$$\frac{\partial \rho}{\partial t} = D\,\Delta\rho \qquad (4)$$

with the condition :

$$\rho(t=0) = \delta(\vec{r}) \qquad (5)$$

is given by :

$$\rho(x,y;t) = \frac{1}{4\pi D t} \exp -\left(\frac{x^2+y^2}{4Dt}\right) \qquad (6)$$

It is a satisfactory solution for the diffusion on the sphere when the

following conditions are fulfilled :

$$\sqrt{\langle x^2 \rangle} \ll 1 \qquad (7)$$
$$\sqrt{\langle y^2 \rangle} \ll 1$$

i.e. when

$$\sqrt{2Dt} \ll 1 \qquad (7')$$

In the neighborhood of Ω, however, this planar diffusion approximation is valid up to much longer times, since the density in this zone originates from molecules which have made only small excursions over the sphere.

More precisely, for $Dt = 0.2$ ($\sqrt{2Dt} = 0.63$), the approximation (6) underestimates the density ρ and its Laplacian $\Delta\rho$ at the origin by a factor 0.935 which is quite close to one. This approximation becomes therefore very attractive when one realises that as soon as $\omega_D\tau$ is much greater than unity (as it always is in the conditions for which a resolved stimulated echo is observed) the most important contributions in (3) arise from molecules for which $|[P_2(\Omega)-P_2(\Omega')]| < \frac{1}{\omega_D\tau}$, the other contributions being washed out by the oscillations of the cosine function.

With the choice of coordinates given in figure (2), the quantity $[P_2(\Omega)-P_2(\Omega')]$ appearing in (3) can then be approximated in the neighborhood of Ω by :

$$\left[P_2(\Omega) - P_2(\Omega')\right] \approx 3 \sin\alpha \cos\alpha \, y \qquad (8)$$

Within the planar diffusion approximation, the integration over $d\Omega'$ involved in (3) can now be readily performed using standard results on gaussian averages. One is then left with

$$A_{\substack{\text{planar} \\ \text{diffusion}}}(\tau, t_w) = \int \frac{d\Omega}{4\pi} \exp - \left\{ 9(\omega_D\tau)^2 \sin^2\alpha \cos^2\alpha \frac{\langle y^2 \rangle}{2} \right\} \quad (9)$$

with

$$\langle y^2 \rangle = 2Dt_w$$

$A_{pl.d.}(\tau,t_w)$ reduces to a function $f(\lambda)$ (plotted in figure (3)) of the variable $\lambda = 9(\omega_D\tau)^2 Dt_w$:

$$A_{\substack{\text{planar}\\ \text{diffusion}}}(\tau,t_w) = f(\lambda) = \int_0^1 \exp -\{\lambda u^2(1-u^2)\}\, du \qquad (10)$$

The damping factor is equal to 1/2 for $\lambda=6.18$, i.e. for $(\omega_D\tau)^2 Dt=0.69$. At large λ, it approaches zero asymptotically with a power law :

$$f_{as.}(\lambda) = \frac{1}{2}\sqrt{\frac{\pi}{\lambda}} \qquad (11)$$

In order to test the accuracy of the planar diffusion approximation, we have performed a Monte Carlo calculation of the motional damping factor $A(\tau,t)$. For that purpose, rotational brownian motions were generated and their contributions to (3) averaged until the statistical error became negligible.

For $\omega_D\tau=5$, one can see on figure 4(a) that the exact value of the damping $A(\tau,t)$ is very close to the value given by the planar diffusion approximation up to $Dt=0.2$. Significant differences appear only for values of $\omega_D\tau$ less than 3, as shown in fig.4b.

In conclusion, the comparison of the results of the Monte Carlo simulation with the planar diffusion approximation shows that the later provides a satisfactory quantitative description of the damping of St.E. induced by a rotational diffusion motion within limits which contain most of experimental situations of interest.

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FIGURE CAPTIONS

Fig.1 Formation of a stimulated echo following a three pulse R.F. sequence as explained in the text. The shapes of the signals correspond to a powdered sample of solid $^{15}N_2$ at low temperature.

Fig.2 Definition of the frame (x,y) in the plane π tangent to the sphere at Ω.

Fig.3 The St.E. damping factor as given by the planar diffusion approximation as a function of the reduced variable $\lambda=9(\omega_D\tau)^2Dt$.

Fig.4 Comparison between the St.E. damping factor as given by the planar diffusion approximation (dashed line) and the exact result (full line) obtained from Monte Carlo simulations for different values of $\omega_D\tau$.

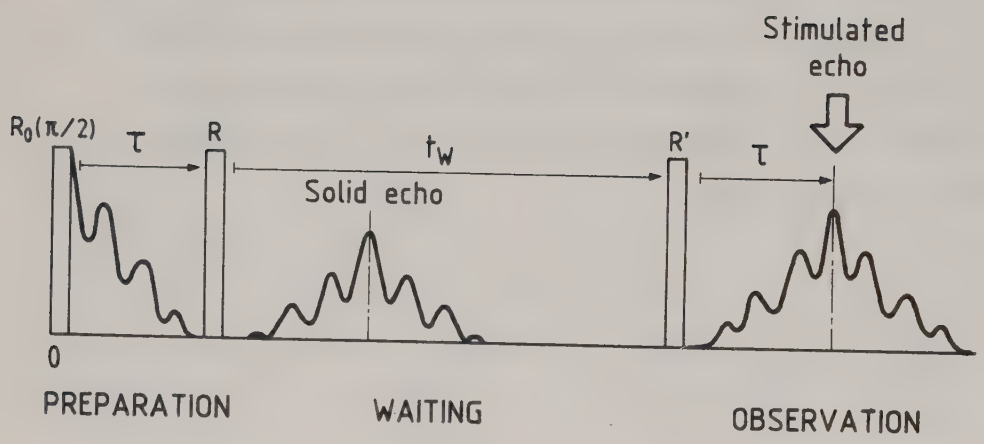

Stimulated
echo
$R_0(\pi/2)$
τ
R
t_w
R'
τ
Solid echo
0
PREPARATION
WAITING
OBSERVATION

Fig. 1

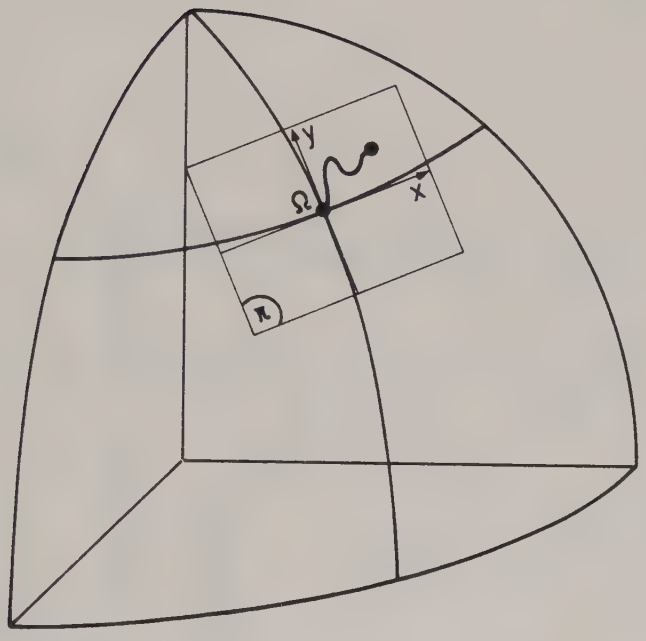


Fig.2

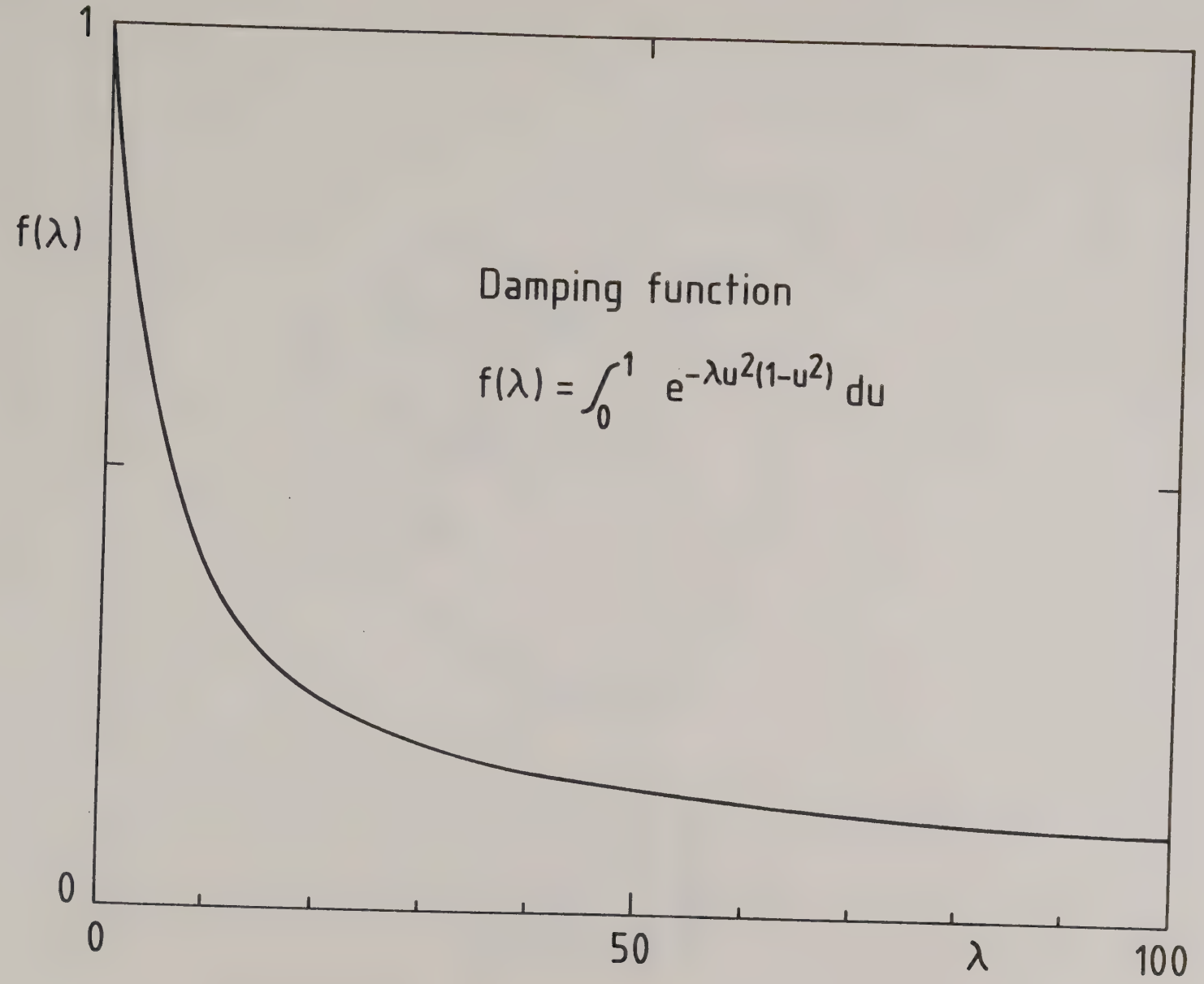

1
f(λ)
Damping function
$f(\lambda) = \int_0^1 e^{-\lambda u^2(1-u^2)}\, du$
0
0
50
λ
100

Fig.3

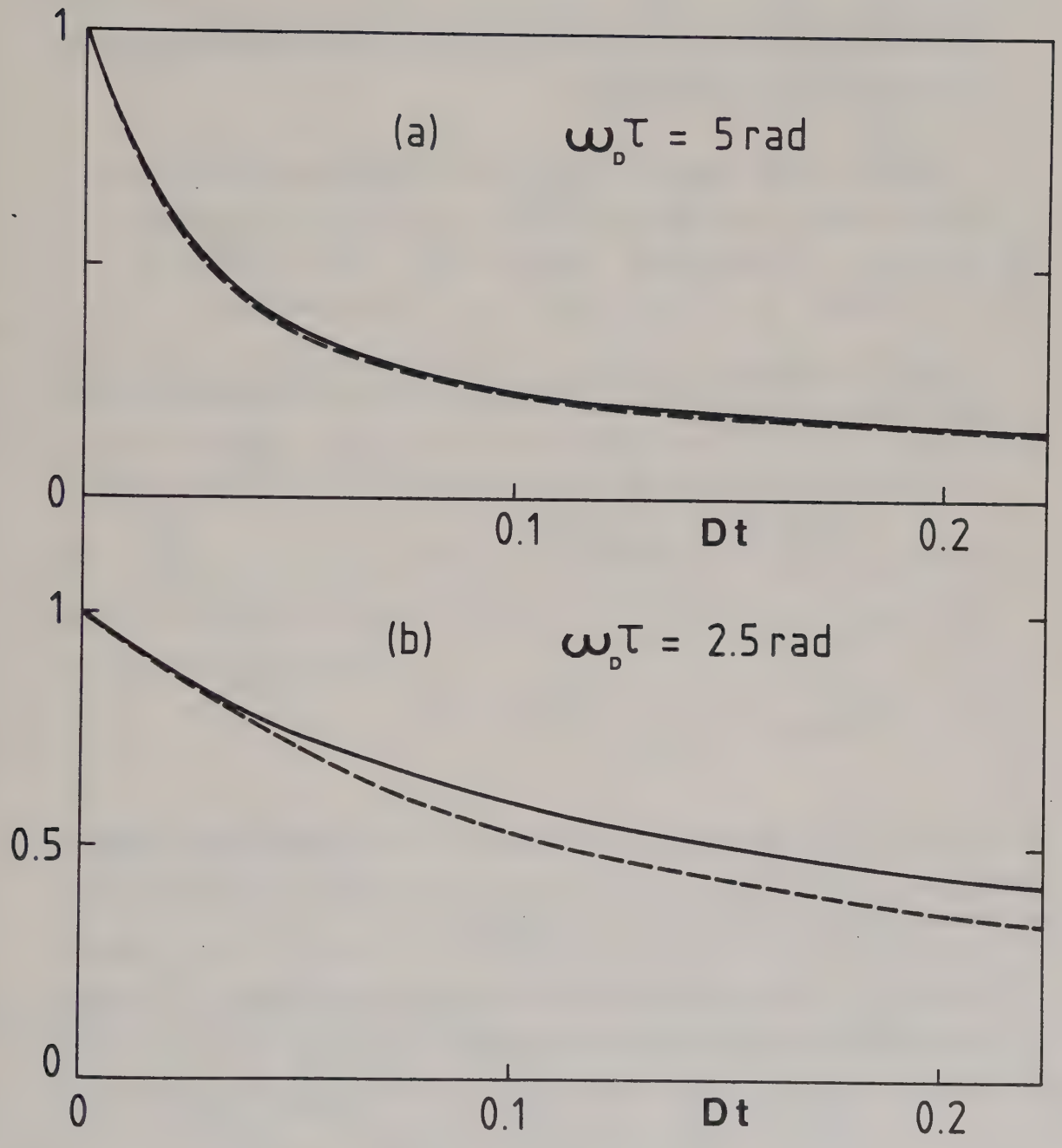


Fig. 4

COMPLEMENTS

LE MOUVEMENT BROWNIEN DE ROTATION D'UNE TIGE ET LE ET LE ROTATEUR QUANTIQUE.

Pour un rotateur libre, l'équation de Schrödinger et l'équation de diffusion sont formellement identiques : leurs fonctions propres sont simplement les harmoniques sphériques $Y_{\ell m}$. Cette identité de structure entraîne une analogie profonde des deux situations.

Ainsi, la fonction de partition d'une molécule d'hydrogène ortho (l impair) est donnée par :

$$Z_{impair} = \sum_{\ell\ impair} (2\ell+1)\, e^{-\ell(\ell+1)\frac{B}{T}}$$

et celle d'une molécule para vaut :

$$Z_{pair} = \sum_{\ell\ pair} (2\ell+1)\, e^{-\ell(\ell+1)\frac{B}{T}}$$

Ce sont les valeurs de ces deux fonctions qui fixent à l'équilibre les proportions d'ortho et de para hydrogène. Quels sont les analogues de ces quantités pour un mouvement de diffusion ?

Pour Z_{pair} , cet analogue est simplement la fonction de corrélation $g(t)$ de la densité pour le mouvement de diffusion d'une tige :

$$g(t) = \frac{1}{2\pi} \sum_{\ell\ pair} (2\ell+1)\, e^{-\ell(\ell+1)Dt}$$

avec la correspondance $Dt \equiv \frac{B}{T}$.

Pour Z_{impair}, il faut considérer la fonction de corrélation du mouvement de diffusion d'une tige portant une densité positive à un bout et négative à l'autre bout.

Cette analogie fournit alors une interprétation simple du résultat analytique suivant que nous avons obtenu avec M. Goldman dans la limite des hautes températures :

$$\frac{Z_{pair} - Z_{impair}}{Z_{pair} + Z_{impair}} \underset{T\to\infty}{\sim} \frac{-\pi^{3/2}}{\sqrt{\frac{B}{T}}} e^{-\frac{\pi^2}{4\left(\frac{B}{T}\right)}}$$

Les fonctions de corrélation des deux types de tiges ne diffèrent en effet aux temps courts que d'un terme proportionnel à la probabilité de retournement de la tige (soit un parcours de longueur π) : dans un espace à deux dimensions, cette probabilité est proportionnelle à $\exp -\left(\frac{\ell^2}{4DT}\right)$; si l'on utilise la correspondance $Dt \equiv \frac{B}{T}$, on retrouve bien le terme non analytique en $\frac{1}{T} e^{-\pi^2/4(B/T)}$ (on peut aussi évaluer le préfacteur).

3) RMN ET MOUVEMENT

Nous présentons sur le tableau C1 ci-contre les conséquences du mouvement sur les formes de raie RMN et les divers types d'échos. Il s'agit ici de molécules classiques* agitées d'un mouvement aléatoire de rotation de temps caractéristique t_m. Nous rappelons ci-dessous la signification des fréquences et temps qui apparaissent dans les fréquences caractéristiques.

- D : échelle des interactions nucléaires intramoléculaires
- d : " " " intermoléculaires
- τ : temps de préparation
- t_w : temps d'attente
- $t_{ds(\tau)}$: temps de diffusion spectrale

---

*supposées ne pas présenter de déplacement chimique anisotrope pour simplifier.

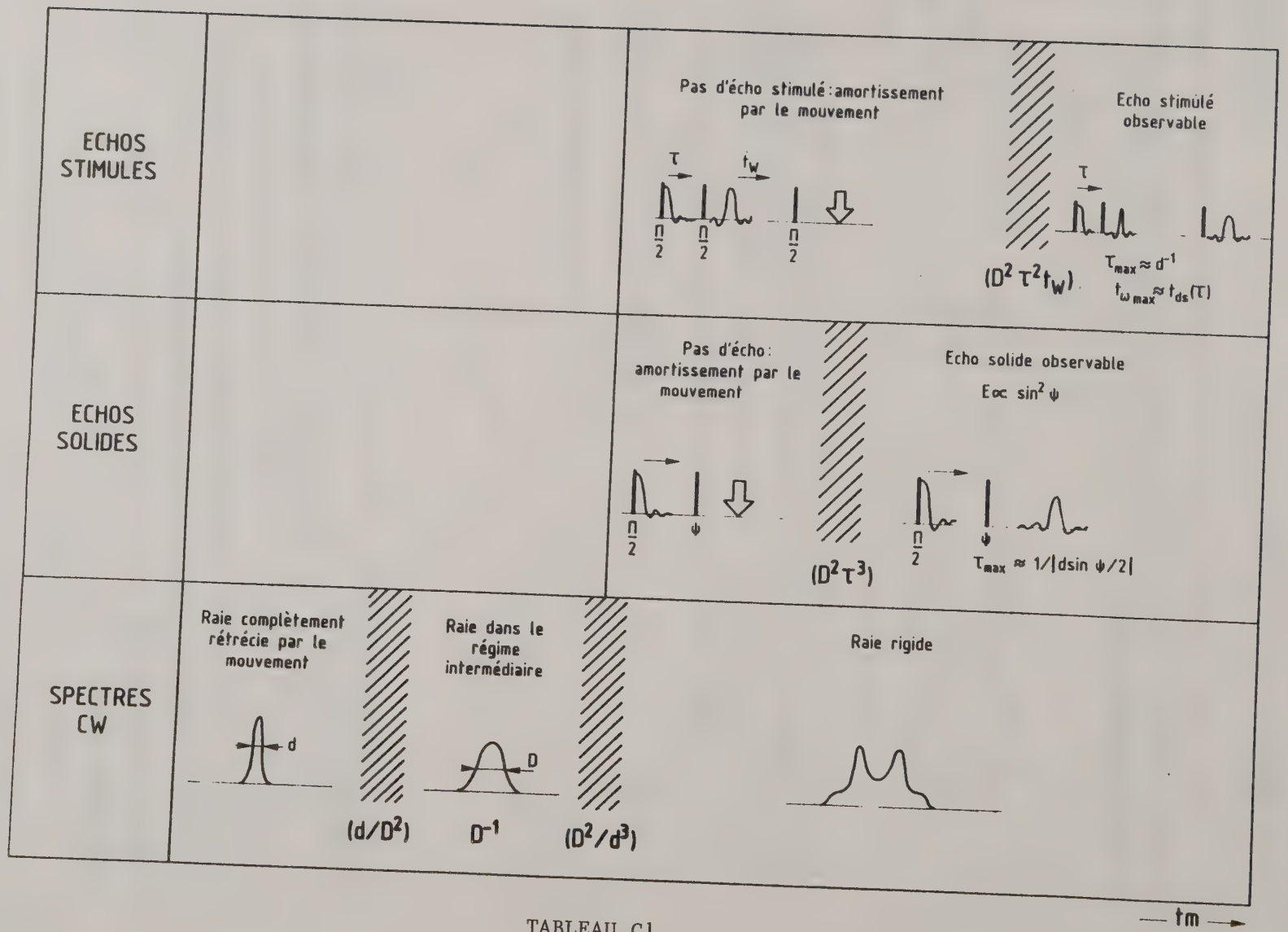

ECHOS STIMULES
Pas d'écho stimulé : amortissement par le mouvement
τ
t_w
π/2
π/2
π/2
Echo stimulé observable
τ
$\tau_{max} \approx d^{-1}$
$t_{\omega max} \approx t_{ds}(\tau)$
$(D^2 \tau^2 t_w)$
ECHOS SOLIDES
Pas d'écho : amortissement par le mouvement
π/2
ψ
Echo solide observable
$E \propto \sin^2 \psi$
π/2
ψ
$\tau_{max} \approx 1/|d \sin \psi/2|$
$(D^2 \tau^3)$
SPECTRES CW
Raie complètement rétrécie par le mouvement
d
Raie dans le régime intermédiaire
D
Raie rigide
(d/D^2)
D^{-1}
(D^2/d^3)
tm

TABLEAU C1

IV - RELAXATION LONGITUDINALE ET FLUCTUATIONS ORIENTATIONNELLES

Comme indiqué dans l'introduction de cette partie, les termes non séculaires de l'hamiltonien de couplage entre les noyaux et les degrés de liberté orientationnels sont une source de relaxation pour l'aimantation nucléaire longitudinale. L'étude de cette relaxation fournit donc des informations sur la dynamique des molécules, et plus précisément sur la densité spectrale des fluctuations orientationnelles à la fréquence de Larmor ω_o ainsi qu'à $2\omega_o$.

Nous établissons ici le lien entre la relaxation longitudinale et la dynamique lorsque les molécules sont dans des états orientationnels bien définis. Nous considérons le cas de molécules d'hydrogène ortho (J=1) ; les notations sont celles du paragraphe II.

L'hamiltonien de couplage est donné par :

$$H = \hbar \sum_i \left\{ D \, \mathcal{D}^{(H)}_{im} \, T^{+}_{im} - c \; I_i . J_i \right\}$$

avec $\frac{D}{2\pi} = 174\,kHz$ $\qquad$ $\frac{c}{2\pi} = 114\,kHz$

Le terme spin-orbite de valeur moyenne nulle ("quenching" du moment orbital) ne contribue pas à la forme de raie RMN mais peut contribuer à la relaxation.

L'hamiltonien H_c étant une somme de termes à une molécule, les aimantations locales I_{z_i} relaxent de façon indépendante. Nous supposerons que la diffusion spectrale dans la raie est bloquée sur l'échelle de temps de la relaxation longitudinale : chaque molécule a alors son propre taux de relaxation T_1^{-1}. L'application du second théorème fluctuation-dissipation [K66] établit le lien suivant entre le taux de relaxation (≡ dissipation) et les densités spectrales des fonctions de corrélation (≡ fluctuations) [A61] :

$$T_1^{-1} = T_{1D}^{-1} + T_{1C}^{-1}$$

avec

$$T_{1D}^{-1} = \frac{D^2}{2}\left[J_{21}(\omega_0) + 4 J_{22}(2\omega_0) \right]$$

$$T_{1C}^{-1} = \frac{C^2}{2} J_{11}(\omega_0)$$

$$J_{2m}(\omega) = \int_{-\infty}^{\infty} \langle \mathcal{H}_m(t)\, \mathcal{H}_m^{+}(0) \rangle e^{i\omega t} dt$$

$$J_{1m}(\omega) = \int_{-\infty}^{\infty} \langle J_m(t)\, J_m^{+}(0) \rangle e^{i\omega t} dt$$

On peut faire aux temps longs l'hypothèse de découplage suivante :

$$\lim_{t\to\infty} \langle \mathcal{H}_m(t)\, \mathcal{H}_m^{+}(0) \rangle = |\langle \mathcal{H}_m \rangle|^2$$

Ces valeurs moyennes s'expriment simplement en fonction de la quadrupolarisation x de la molécule et de l'angle γ entre l'axe Oz et sa direction de quadrupolarisation. Il est alors naturel d'introduire les densités spectrales réduites dans le repère local ainsi définies :

$$j_{2m}(\omega) = \int_{-\infty}^{\infty} \langle \theta_m(t)\, \theta_m^{+}(0) \rangle e^{i\omega t} dt$$

avec

$$\theta_m = \underset{(\text{local})}{\mathcal{H}_m} - \langle \underset{(\text{local})}{\mathcal{H}_m} \rangle$$

On peut alors exprimer le taux de relaxation en fonction :

- de la quadrupolarisation x
- de la position des transitions de la molécule dans la raie RMN ($y = \frac{P_2(\gamma)}{x}$)
- des densités spectrales réduites dans le référentiel local.

On obtient :

$$T_1^{-1}(\omega) = \frac{D^2}{12}\left[\begin{array}{l}(1-x)(1+2x)\left\{\frac{2}{3}(1+y-2y^2)j_{20}(\omega)+\frac{4}{3}(1-y)^2 j_{20}(2\omega)\right.\\ +\left(1+\frac{x}{2}\right)\left\{\frac{2}{9}(2-y+8y^2)j_{21}(\omega)+\frac{4}{9}(8-4y+4y^2)j_{21}(2\omega)\right\}\\ +(1-x)\left\{\frac{4}{9}(2-y+y^2)j_{22}(\omega)+\frac{4}{9}(7+10y+y^2)j_{20}(2\omega)\right\}\end{array}\right]$$

$$+\frac{c^2}{9}\left[(1-x)(1+2y)j_{10}(\omega)+2(2+x)(1-y)j_{11}(\omega)\right]$$

La relaxation est donc inhomogène même lorsque les densités spectrales réduites $j_{\ell m}(\omega)$ sont identiques. On peut à ce stade introduire diverses hypothèses simplificatrices pour pouvoir utiliser la formule ci-dessus. Les résultats que l'on obtient présentent toujours les caractéristiques suivantes :

- La relaxation de chaque composante de la raie RMN est non exponentielle

- Le taux de relaxation décroît avec l'écart en fréquence avec le centre de la raie. (Ce sont les molécules désordonnées du centre du spectre qui ont la plus grande amplitude de fluctuation).

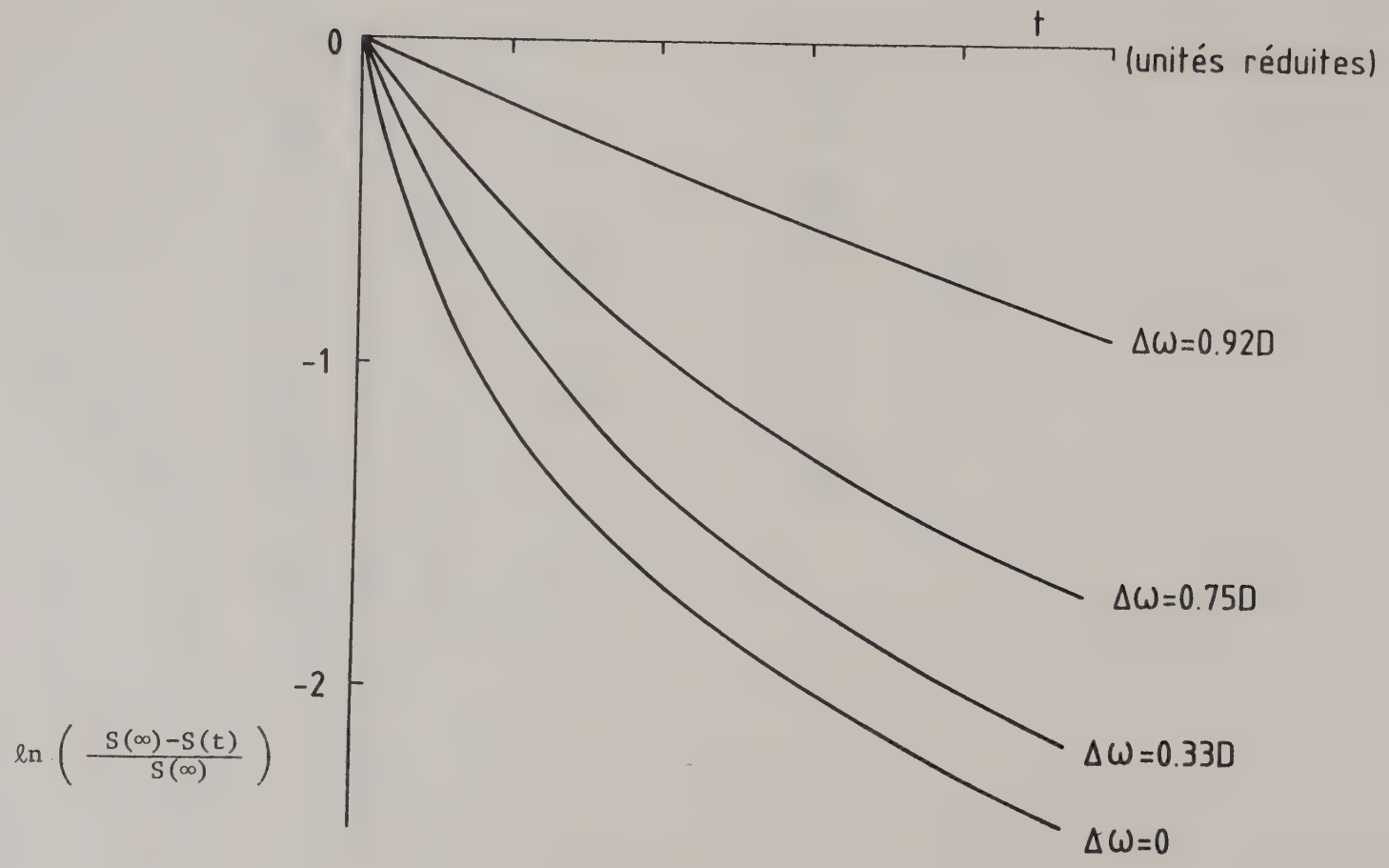
La figure C1 montre les relaxations de différentes parties de la raie RMN calculées avec les hypothèses suivantes :

- $j_{\ell 1}(\omega)$, $j_{\ell 2}(\omega) \ll j_{\ell 0}(\omega)$ pour $\omega=\omega_o$, $2\omega_o$. Cette hypothèse serait exacte pour une molécule dans un gradient de champ électrique à basse température.

- $j_{20}(\omega) = j_{10}(\omega)$.

Le rapport $j_{20}(2\omega_o)/j_{10}(\omega_o)$ a été pris égal à 1 et la distribution de quadrupolarisations P(x) correspond à un spectre typique d'hydrogène vitreux (X_{ortho} = 0.53, T = 220mK).

Ces courbes de relaxation reproduisent le comportement de la relaxation dans l'hydrogène solide en fonction de la position dans la raie RMN [WYM82]. Il subsiste cependant encore trop d'inconnues pour autoriser une discussion des résultats expérimentaux dans le cadre développé ici et extraire alors des données dynamiques précises sur l'hydrogène solide.



C1 - Courbes de relaxation calculées du signal CW
pour plusieurs écarts Δω au centre du spectre après saturation.

PARTIE D :

ETUDE RMN DE L'AZOTE $^{15}N_2$

INTRODUCTION

I - LA DIFFUSION DANS L'AZOTE SOLIDE

II - L'ORDRE ORIENTATIONNEL EN PHASE HEXAGONALE

III - LA RMN DE $^{15}N_2$ ORDONNÉ EN PHASE α

Cette partie rassemble les résultats expérimentaux que nous avons obtenus sur l'azote $^{15}N_2$ pur. Elle contient une étude de la diffusion dans le solide qui n'avait pu être menée à bien dans $^{14}N_2$ (§I), une étude de l'ordre orientationnel en phase hexagonale (§II) et une étude de l'ordre orientationnel en phase cubique (§III).

I - LA DIFFUSION DANS L'AZOTE SOLIDE

ARTICLE :

" NMR STUDY OF SELF-DIFFUSION IN SOLID N_2 "

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Pergamon Press Ltd. 1981. Printed in Great Britain.

0038-1098/81/330969-03$02.00/0

N.M.R. STUDY OF SELF-DIFFUSION IN SOLID N_2

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From the measurement of the N.M.R. relaxation times T_2 in $^{15}N_2$ and in $^{14}N_2$ containing Ar impurities we extract the self diffusion coefficient D in h.c.p. N_2. We find that self-diffusion is a thermally activated process with an activation enthalpy $\Delta H^*/k = 1030 \pm 25$ K. We discuss the diffusion process and conclude that it can be related to the motion of thermally activated vacancies.

INTRODUCTION

Self-diffusion is a common phenomenon in most solids[1], at least in the vicinity of the melting point. In general, the migration of the particules forming the solid is induced by the rapid random motion of a few point defects, usually vacancies. In simple Van der Waals solids, such as rare gas solids[2] or the molecular solids H_2 [3-5] and D_2 [5-7], models taking this mechanism into account predict self-diffusion coefficients D in close agreement with the measured values. Experimentally, D may be determined in two very different ways : the radioactive tracer method and the measurement of the N.M.R. relaxation rates T_1, $T_{1\rho}$ and T_2. In h.c.p. $^{14}N_2$ (^{14}N : I=1 is the common isotope) the relaxation induced by the diffusion is completely swamped by another mechanism[8].

We have thus been led to measure the transverse relaxation time T_2 in h.c.p. $^{15}N_2$ (^{15}N : I=1/2) for which such a limitation is circumvented. In order to obtain further insight into the diffusion process we have also measured T_2 in $^{14}N_2$ containing a few Ar impurities : in this system the transverse relaxation is dominated by the perturbation of ^{14}N nuclei N.M.R. frequencies during the encounters between a N_2 molecule and an Ar atom, and therefore depends strongly on the diffusion rate.

N.M.R. transverse relaxation and self-diffusion

From the motional narrowing[9] of the intermolecular dipolar linewidth one extracts the mean time τ that a molecule stays on a site of the lattice. (In h.c.p. N_2 the intramolecular dipolar linewidth is almost completely narrowed by the rotational motion[8] in the temperature range of our study). In the adiabatic case ($\omega_o\tau >> 1$) and in the extreme narrowing regime ($T_2 >> T_{2\text{Rigid lattice}}$), the random walk theory of Torrey[10] (refined by Sholl et al.[11,12] for cubic crystals) gives for the h.c.p. lattice in the case of a polycrystalline sample :

$$T_2^{-1} = 212 \left(\frac{3}{10}\right) \frac{\gamma^4 \hbar^2 c I(I+1)}{8a^6} \tau \qquad (1)$$

where a is the lattice parameter ($a \simeq 4.10$ Å in N_2[13]) and c the concentration of the magnetic species of spin I and nuclear magnetogyric ratio γ. In h.c.p. $^{15}N_2$ the magnetic species are the ortho-molecules ($\vec{I} = 1$, antisymmetric orbital wave function) with a concentration c = 3/4. The para-molecules (I=0, symmetric orbital wave function) are not observed by N.M.R.

In fact, molecules which diffuse via vacancies do not have a random walk and successive jumps are correlated.

A complete theory of N.M.R. relaxation taking these correlations into account has been developed by Wolf[14-16] in the case of cubic crystals. He shows that Torrey's results may be in error by an amount of 30%.

The value of the self-diffusion coefficient in the case of isotropic random jumps is related to τ by the Einstein relation $D = \ell^2/6\tau$ (2) where ℓ is the length of an elementary jump. For vacancy induced diffusion, this relation is only approximate and a correlation factor[2,17,18] has to be introduced; formula (2) is however currently used to estimate D.

Self diffusion is in most cases a thermally activated process. In the case of the vacancy induced mechanism[1,18], the time τ is of the form $\tau = \tau^o \exp(\Delta H^*/kT)$ with an activation enthalpy ΔH^* which is the sum of the formation enthalpy and of the migration enthalpy of vacancies. It then follows from (1) that $T_2 = T_2^o \exp(-\Delta H^*/kT)$ and from (2) that $D = D^o \exp(-\Delta H^*/kT)$. The parameters ΔH^*, τ^o and D^o describing the diffusion are therefore readily deduced from T_2 values.

Experiments in $^{15}N_2$

Our pulse spectrometer was operated at a Larmor frequency $\nu_o \simeq 3$ MHz. The relaxation time T_2 was deduced from the exponential decay of the echoes following a two pulse sequence. In the extreme narrowing regime (solid line of the curve in fig. 1), T_2 closely follows the expression :

$$T_2 = 39.10^6 \exp\left(-\frac{1030}{T}\right) \text{ s}$$

The related time τ (given by the right hand scale of fig. I) is :

$$\tau = 17.10^{-14} \exp\left(\frac{1030}{T}\right) s$$

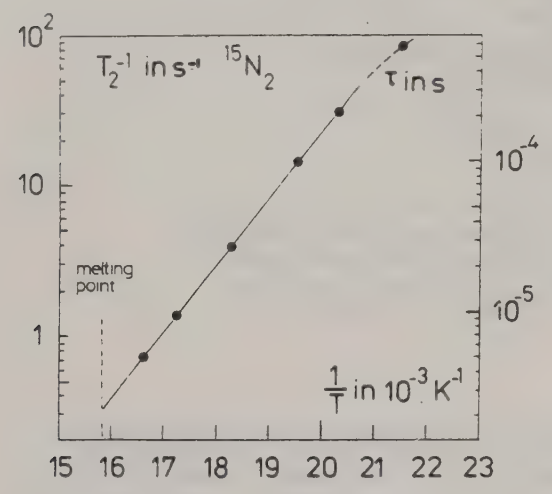

Fig.1. Relaxation rates T_2^{-1} in $^{15}N_2$ and the related times τ in the extreme narrowing regime (solid line).

The activation enthalpy is determined with the accuracy $\Delta H^*/k = 1030 \pm 25$ K. The determination of the preexponential factor τ^o is less precise and we estimate $\tau_o = 17 \pm 9\ 10^{-14}$ s. The self-diffusion coefficient is then :

$$D = 16^{+13}_{-5}.10^{-8} \exp\left(-\frac{\Delta H^*}{kT}\right) m^2.s^{-1}$$

DISCUSSION

The activation enthalpy ΔH^* has been widely studied in relation to the thermodynamic properties of solids and empirical laws[18], with a partial theoretical support, have emerged. The most simple one is the Van Liempt relation[19] which states $\Delta H^*/k \approx 16.1$ Tm, where Tm is the melting temperature. This relation is well obeyed in closed packed metals[20] when diffusion is known to occur by a vacancy mechanism and has been applied with some success to molecular crystals[18]. For N_2, this relation predicts $\Delta H^*_{V.L.}/k = 1015$ K, which is close to the experimental value.

Another fruitful concept is the law of corresponding states[21] when it is applied to solids belonging to the same family, for example the rare gas family[2]. In this way, N_2 may be compared (see table I) to H_2 and D_2 which have similar phase diagrams and lattice structures. Although the predictions concerning ΔH^* are uncertain because of the high De Boer quantum parameters of H_2 and D_2, one can relate the order of magnitude of the preexponential factor D^o found in N_2 to those in H_2 and D_2 : the law of corresponding states predicts that D^o varies as $\sigma\sqrt{\varepsilon}/m$, where ε and σ are the Lennard-Jones parameters of the intermolecular potential. This factor is roughly the same for H_2, D_2 and N_2, and one therefore expects that the experimental values of D^o (quoted in table I) do indeed have the same magnitude. This common value ($D^o \approx 10^{-7}$)

Table I

	$\frac{\Delta H^*}{k}$ (K)	$\frac{\Delta H^*}{kTm}$	$10^8.D^o$
H_2	200 ± 10[197]	14.3	30 ± 15 [6]
D_2	280 ± 10[290]	15	4^{+4}_{-2} [7]
N_2	1030 ± 25	16.3	16^{+13}_{-5}

Comparison of the diffusion parameters $\frac{\Delta H^*}{k}$ (K) and $D^o(m^2.s^{-1})$ of H_2 [3.4], D_2 [6.7] and N_2. The theoretical values of Ebner and Sung [5] obtained from a vacancy mechanism are quoted between brackets.

is smaller than usual values[18] in metals ($D^o \approx 10^{-4}$-10^{-3}), in rare gas solids ($D^o \approx 10^{-4}$) and in plastic crystals ($10^{-5} < D^o < 10^{4}$).

Finally, let us mention that the mass difference between $^{15}N_2$ and $^{14}N_2$ affects only D^o (and not ΔH^*) and is expected to be small[18].

T_2 measurements in $^{14}N_2$ containing Ar impurities

We have observed, in solid h.c.p. $^{14}N_2$ containing Ar impurities, that the N.M.R. linewidth of ^{14}N nuclei in the vicinity of Ar atoms is increased by an important factor : the lattice is locally distorted near an Ar impurity and the coupling between the resulting electric field gradient and the quadrupolar moment of ^{14}N nuclei (I=1) shifts their resonance frequencies. However, near the melting point, the relative diffusion of Ar atoms and N_2 molecules causes a motional narrowing of this perturbation. We show in the Appendix that, in the case of weak collisions, the decay of the echoes is exponential and that the relaxation rate (allowing for corrections due to the T_1^{-1} relaxation rate and neglecting correlations between jumps as is done in the Torrey-Sholl theory) is proportional to a time τ_R defined by $\tau_R^{-1} = \tau_{N_2}^{-1} + \tau_{Ar}^{-1}$, where $\tau_{N_2} = \tau$ and τ_{Ar} are defined as before. One can see in fig.2 that $(T_2^{-1} - T_1^{-1})$ follows a thermal activation law in the weak collision regime, with an activation enthalpy $\Delta H^*_R/k = 1080 \pm 80$ K in agreement with the value measured in $^{15}N_2$ $\Delta H^*/k = 1030 \pm 25$ K.

This fact may be related to the diffusion mechanism : in crystals, when the impurities diffuse also via vacancies, it is known[1] that the impurity diffusion coefficient $D_{imp.}$ cannot exceed by more than a small factor the self-diffusion coefficient D of the host, even if an impurity has a greater probability to jump into a neighbouring vacancy than a host molecule. The reason is that an impurity must wait for the passage of a vacancy in order to move. Since an Ar atom is smaller than a N_2 molecule (if one compares the hard core parameters σ) one then expects that Ar impurities are effectively more mobile than N_2 molecules, ($\tau_{Ar}^{-1} > \tau^{-1}$) but that the activation enthalpy describing their motion

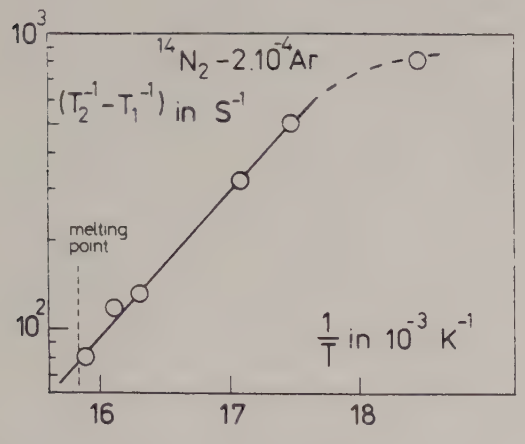

Fig.2. Relaxation rates in $^{14}N_2$ containing Ar impurities (200 ppm). The weak collision regime corresponds to the solid curve.

is the same[1] as for N_2. Within the approximation that correlations between jumps may be neglected, we obtain therefore that ΔH^* has to be the same for both experiments. Hence, the fact that the activation enthalpy determined from τ_R is the same as the one determined from τ supports the vacancy mechanism hypothesis. An interstitial process, for example, is ruled out.

CONCLUSION

Self-diffusion in h.c.p. N_2 is a thermally activated process with an activation enthalpy $\Delta H^*/k = 1030 \pm 25$ K which has been determined using two very different methods. The comparison with self-diffusion in H_2 and D_2 leads to a vacancy mechanism for the diffusion process, and this interpretation is supported by the study of the relative diffusion of Ar impurities and N_2 molecules in $^{14}N_2$.

APPENDIX

The amplitude of an echo occuring at time 2t is given by the average[22] :

$$E(2t) = \langle \exp\{-i(\int_t^{2t} - \int_o^t)\}\omega(t')dt' \rangle$$

where $\omega(t')$ is the instantaneous frequency shift which occurs in the neighbourhood of an Ar impurity. $\{(\int_t^{2t} - \int_o^t)\ \omega(t')\ dt'\}$ represents the total phase shift φ induced by the encounters with Ar atoms between time O and time 2t. The average number n of these encounters is proportionnal to 2t, to the Ar concentration x and to the relative diffusion coefficient D_R. If one neglects correlations between jumps, D_R is given by :

$$D_R = \frac{a^2}{6}\ \tau_R^{-1} = \frac{a^2}{6}\ (\tau_{Ar}^{-1} + \tau^{-1})$$

On the other hand, the mean square of the collision phase shift $\langle \delta\varphi^2 \rangle$ during an encounter is proportional to τ_R^2. When the number of encounters n is high, φ has a gaussian distribution and the average is readily performed :

$$E(2t) = \langle \exp - i\varphi \rangle = \exp - \frac{\langle \varphi^2 \rangle}{2} = \exp\ (-n\ \frac{\langle \delta\varphi^2 \rangle}{2})$$

It then follows from $n \propto 2tx\tau_R^{-1}$ and $\langle \delta\varphi^2 \rangle \propto \tau_R$ that

$$E(2t) = \exp(-x\ t\ \tau_R\ \omega_c^2)$$

where ω_c represents the strength of the perturbation introduced by an Ar impurity. The echo decay is exponential and the relaxation rate due to the diffusion is proportional to τ_R.

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II - L'ORDRE ORIENTATIONNEL EN PHASE HEXAGONALE

1) ARTICLE :

NMR STUDY OF THE ORIENTATIONAL PROPERTIES OF HCP $^{15}N_2$

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N.M.R. STUDY OF THE ORIENTATIONAL PROPERTIES OF h.c.p. $^{15}N_2$

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We have observed in h.c.p. $^{15}N_2$ below 42 K an anomalous broadening of the NMR line-shape which we attribute to the onset of a partial orientational ordering much more pronounced than that observed in h.c.p. $^{14}N_2$ (the common isotope). This interpretation of the line broadening is unambigously confirmed by a pulsed NMR study. We discuss how this striking difference between the two solids can be linked to other known differences in their physical properties.

Introduction

Most of the physical properties of solid nitrogen, one of the simplest molecular solids, have been widely investigated and their interpretation has led to the determination of the principal features of the intermolecular potential. Orientational properties, which depend on the anisotropic part of the potential, are not however known in detail and still deserve careful attention. This paper deals with the orientational properties of the hexagonal phase of solid nitrogen (βN_2).

In the low temperature cubic phase (αN_2) ($T < T_o = 35.6$ K), molecular orientations are long-range ordered according to a four-sublattice pattern. This antiferro-orientational Pa 3 structure ensures the minimisation of the leading quadrupole-quadrupole energy term of the anisotropic part of the intermolecular potential. At $T=T_o$, solid nitrogen undergoes a first order transition to the h.c.p. β phase in which molecules are to a large extent orientationaly disordered. Similar phase diagrams occur also for other molecular solids [1,2] such as ortho H_2, para D_2 or CO, for which the quadrupole-quadrupole interactions are also dominant. Whereas βH_2 and βD_2 are true para-orientational phases, there is a large body of experimental evidence which suggests that βN_2, [1,3,8] and probably also β CO [9], are not. Furthermore, it has been surmised [8] that the orientational properties are not identical in $\beta\,^{14}N_2$ and $\beta\,^{15}N_2$ (the lighter isotope ^{14}N is the common one).

The nuclear magnetic resonance (N.M.R.) study of orientational ordering in $\beta^{15}N_2$ we report here strongly confirms this fact and shows that this phase is far less orientationally disordered than previously thought. This paper is organized as follows : A survey of orientational properties of βN_2 is presented in §1. The main features of N.M.R. in $^{15}N_2$ are reported in §2. Experimental results concerning the temperature dependence of respectively the line-width and the solid echoes are given in §3 and §4. We then discuss in §5 how these results can be connected to other properties of $\beta^{15}N_2$, stressing the differences between $\beta^{14}N_2$ and $\beta^{15}N_2$.

1. Orientational properties of βN_2

We first consider $\beta^{14}N_2$ which is better known than $\beta^{15}N_2$. Since the rotational heat capacity C_v^{rot} of $\beta^{14}N_2$ exceeds the heat capacity of free rotators, the rotational motion of the molecules is clearly hindered. A model of correlated rotators [4] has been proposed to account for this excess in the specific heat, which decreases on increasing the temperature. (The picture of a "meshed gear-box" has been proposed to describe the correlations between molecular orientations). One also knows that $\beta^{14}N_2$ sustains librational excitations since the far infrared absorption spectrum [5] shows a clear librational behaviour below 45 K and that a Raman line corresponding to a librational mode has been identified [6]. X-ray diffraction experiments [7] (performed above 50 K only) have been analysed in terms of a free precession model, in which the molecular axes rotate around the $\hat{c}$ axis of the h.c.p. lattice at a given precession angle $\theta_p = 36° \pm 2.5°$ close to the magic angle $\theta_m = 54.74°$. An alternative model in which molecules librate and execute random jumps among discrete minima of the potential still close to the magic angle has been considered [1,7] and would fit the X-ray data equally well. Both precession models around the $\hat{c}$ axis have a symmetry in agreement with the interpretation of the Raman spectrum [6], the second model being favoured by a geometrical analysis [10] which shows that continuous precession would lead to a slight overlapping of external electronic shells of neighbouring molecules. This however artificial precession picture has been criticized, and it has been argued [11] that the X-ray intensities could be fitted by any model in which the orientational order parameter P, defined by the following average, is small :

$$P = \langle P_2(\gamma) \rangle = \left\langle \frac{3\cos^2\gamma - 1}{2} \right\rangle \qquad (1)$$

where γ is the angle between a molecular axis $\hat{\zeta}$ and the $\hat{c}$ axis of the h.c.p. lattice. More precisely, a limit $|p| < 0.09$ can be inferred from the data analysis. A much more stringent limit has been deduced from the measurement of the residual average electric field gradient seen by ^{14}N

nuclei [8](^{14}N:nuclear spin I=1). Since this E.F.G. is essentially of intramolecular origin, its average is directly proportional to the order parameter p. One obtains in this way a value for p always less than 10^{-3} in the phase which decreases on lowering the temperature and becomes unobservably small below 44K.

Far less information concerning $\beta^{15}N_2$ is available in the literature. A recent X-ray study [12] of the crystallographic parameters has however shown very different behaviours of the expansion coefficients in $\beta^{15}N_2$ and in $\beta^{14}N_2$. The authors have obtained the rotational heat capacity C_v^{rot} by using their data together with available C_p data. As it does not display the same rapid decrease on increasing the temperature as found in $\beta^{14}N_2$, they have concluded that orientational ordering is probably not the same in the two nitrogens. Differences between the two solids will be further discussed in §5.

2. Nuclear interactions in solid $^{15}N_2$

As ^{15}N nuclei have a nuclear spin quantum number I = 1/2, there are two species of $^{15}N_2$ molecules : i) para-molecules with total nuclear spin quantum number I=0 and an even symmetry orbital wave function, ii) ortho-molecules with I=1 and an odd symmetry orbital wave function. In N.M.R. experiments, one observes only the ortho-molecules (any effect of conversion may be neglected on the relevant time scale for N.M.R.).

We shall suppose that the rotational motion of each molecule i has a symmetry axis $\hat{\zeta}_i$ making an angle θ_i with the magnetic field $H(H = (\omega_o/|\gamma|)$ which defines the $\hat{z}$ axis. Since the motion around $\hat{\zeta}_i$ is expected to be rapid compared to the characteristic frequency ($\sim 10^3$Hz) of the intramolecular interactions, one has to consider only their motional average.

The relevant part H^o of the secular intramolecular Hamiltonian, which contains a dipolar term and an asymmetric chemical shift term [12], is then given by :

$$H^o = -\mathcal{H} \sum_i \left\{ Dp_i P_2(\theta_i) \left(\frac{3I_{z_i}^2 - 2}{3} \right) + \chi p_i P_2(\theta_i)\, I_{z_i} \right\} \quad (2)$$

with $D = \frac{3}{2} \frac{\gamma^2 \mathcal{H}}{R^3} = 8710$ rad.s^{-1} and

$$\chi = \frac{2}{3} (\sigma_{//} - \sigma_{\perp})\, \omega_o = 4.10^{-6} \omega_o .$$

The degeneracy of the NMR frequencies corresponding to the transitions a) $I_z = 1 \rightarrow 0$ and b) $I_z = 0 \rightarrow -1$ is therefore slightly lifted according to :

$$\omega_{i\ \substack{a \\ b}} = \omega_o - (\chi \pm D)\, p_i P_2(\theta_i) \quad (3)$$

One has also to consider dipolar interactions between spins of different molecules. Since intermolecular distances are much greater than the distance between nuclei of a same molecule, we shall take for the dipolar Hamiltonian h between ortho-molecules the same expression as for (I=1) nuclei localized at the nodes of the lattice. (This approximation leads to an error of less than 10% for the second moment).

These intermolecular dipolar interactions result in a broadening of the fine structure of the line-shape due to the intramolecular interactions. Let us note that if the intramolecular line-width exceeds the characteristic frequency of the intermolecular interactions, a part of the transitions induced by these interactions are quenched since they do not conserve the energy associated with H^o. Secular terms with respect both to the Zeeman Hamiltonian and H^o have only to be considered and it results in a reduction of the second moment of the effective intermolecular interactions (the reduction factor is 0.61 if one supposes that all the molecules of the same crystal have the same symmetry axis $\hat{\zeta}$).

3. N.M.R. line-width in $\beta^{15}N_2$

We have performed N.M.R. on powdered samples of $\beta^{15}N_2$ carefully prepared to avoid strains. (We have checked that samples of $\beta^{14}N_2$ prepared in the same way presented no anomalous quadrupolar broadening of the line-shape due to internal strains or to non-negligible order parameters). Spectra were obtained using a low level Robinson oscillator operating at a frequency of 3 MHz. The temperature dependence of the N.M.R. line-width in $\beta^{15}N_2$ is shown in Fig.1 (full line).

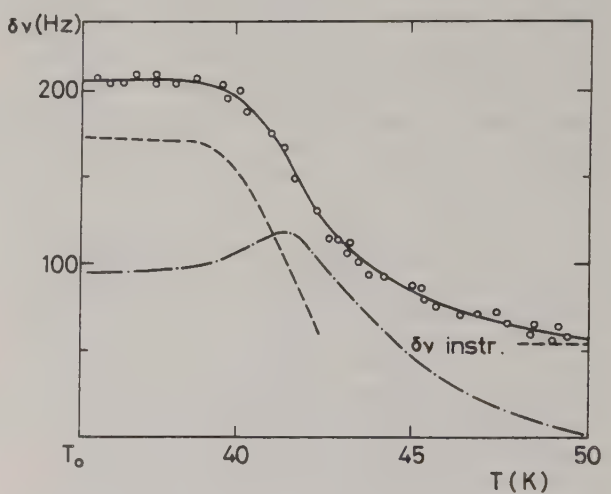

Fig.1. Temperature dependence of the experimental line-width (full line) in $\beta^{15}N_2$. The dashed line and the dot-dashed line represent respectively an estimation of the intramolecular contribution, linked to the onset of orientational ordering, and of the intermolecular contribution.

On lowering the temperature T below the melting point, the N.M.R. line-shape broadens since the intermolecular dipolar linewidth increases as the self-diffusive motion of the molecules slows down. We have estimated the intermolecular dipolar line-width (dot-dashed line in fig.1) using standard motional narrowing theory [13] together with the value of the diffusion rate [14]. This intermolecular broadening is almost complete around T=41.5 K and the lattice can be considered as rigid from the NMR point of view at lower temperatures (The small decrease between 41 K and 39 K has been inferred from the behaviour of solid echoes and is linked to the reduction effect dis-

cussed in §1). Nevertheless, the line-shape still broadens on further lowering the temperature until a plateau is reached at T ≈ 39 K. The second moment of the NMR line shape

$$M_2 = (M_2^{exp} - M_2^{instr.}) \approx 10 \times 10^3 \text{ Hz}^2$$

then exceeds the intermolecular dipolar second moment $M_2^{inter.} \simeq 4.3 \times 10^3$ Hz^2. An estimation of the extra-contribution to the line-width which has to be considered to account for the experimental line-width is given in fig.1 (dashed line). It has has been obtained by assuming that the square of the experimental line-width is the sum of the squares of the line-widths corresponding to the different broadening mechanisms. If one attributes this unexpected contribution to the line-width to an incomplete motional narrowing of the intramolecular interactions due to a residual orientational ordering, one deduces an average order parameter $p^* = \langle p_i^2 \rangle^{1/2} \simeq 0.1$ which is two orders of magnitude greater than that previously found in $\beta^{14}N_2$ [8]. In order to check this interpretation (and to rule out any spurious broadening mechanism such as a field gradient) we have used pulsed NMR methods.

4. Solid echoes in $\beta^{15}N_2$

Solid echoes following a two RF pulse sequence have been observed a long time ago in solid H_2 [15] ($H:I = 1/2$ as ^{15}N) and more recently exploited [16] for the study of orientational ordering in solid H_2 and in solid D_2. Their interest lies in the characteristic dependence of the echo amplitude on the pulse sequence that one obtains when molecules are orientationally ordered.

For $^{15}N_2$ molecules, the predicted solid echo amplitude differs only slightly from the calculated one for H_2 molecules [15], for which the asymmetric chemical shift is negligible. One predicts after the pulse sequence noted $\{\frac{\pi}{2} - \tau - \psi_\varphi\}$ (in which the first pulse corresponds to a $\pi/2$-rotation around the $\hat{y}$ axis and the second one, applied at time τ, to a rotation of angle ψ around an axis lying in the xy plane and at angle φ with the $\hat{y}$ axis) a solid echo whose amplitude E at resonance, and in the absence of intermolecular interactions, is given by :

$$E(2\tau,\psi,\varphi) = e^{2i\varphi} E_1(2\tau,\psi) + E_2(2\tau,\psi) \qquad (4)$$

with :

$$E_1(2\tau,\psi) = \sin^2\psi - \cos\psi(1-\cos\psi)\langle \cos 2Dp_i P_2(\theta_i)\tau \rangle \qquad (4')$$

$$E_2(2\tau,\psi) = \sin^2\psi \langle \exp(-2i\chi p_i P_2(\theta_i)\tau) \rangle \qquad (4'')$$

$$+\cos\psi(1+\cos\psi)\langle \exp(-2i\chi p_i P_2(\theta_i)\tau)\cos(2Dp_i P_2(\theta_i)\tau)\rangle$$

By performing the difference $(E(2\tau,\psi,\pi) - E(2\tau,\psi,0))$ one obtains $E_1(2\tau,\psi)$ alone. This selects the contributions to the echoes that are derived uniquely from the "quadrupolar" terms in the nuclear spin Hamiltonian and depend therefore crucially on the molecular order parameters. An additional magnetic field gradient would leave $E_1(2\tau,\psi)$ unchanged since it corresponds to a vectorial Hamiltonian (of the same form as the asymmetric chemical shift). One can then test the presence of a residual orientational ordering which leads to a noticeable departure of $\langle \cos(2Dp_i P_2(\theta_i)\tau) \rangle$ from its maximum value as soon as $2\tau \sim \frac{1}{D\langle p_i^2 \rangle^{1/2}}$.

Two values of ψ are of special interest :

$$\text{a) } \psi = \frac{\pi}{2}, E_1(2\tau,\tfrac{\pi}{2}) = 1 \qquad (5)$$

$$\text{b) } \psi = \tau, E_1(2\tau,\pi) = 2\langle \cos(2Dp_i P_2(\theta_i)\tau \rangle$$

A direct interpretation of the experimental amplitudes $E_1'(2\tau,\psi)$ according to equation (4') cannot however be carried out, since intermolecular interactions cannot be neglected for long times 2τ. These interactions result in a damping of the solid echoes, and it is known that this damping depends on the rotation angle ψ of the second pulse [17-18]. In particular, the damping is suppressed at short times for $\psi = \pi/2$ (this is another facet of the solid echo effect [17]). In $\beta^{15}N_2$ this damping depends furthermore on the temperature since motional narrowing of the intermolecular line-width decreases as the self-diffusive motion slows down on cooling. Nevertheless, this cannot explain the differences between $E_1'(2\tau,\pi/2)$ and $E_1'(2\tau,\pi)$ which appear in the temperature range 42.5 K → 39 K as is shown in fig.2. The existence at 39 K of a solid echo $E_1'(2\tau,\pi/2)$ with a damping factor of 0.5 for 2τ = 7ms implies that this value of 2τ is not greater than the characteristic damping time T_2 associated with the intermolecular interactions [18]. In this case $E_1'(2\tau,\pi)$ cannot be unobservably small for 2τ > 6ms without implying an almost complete decay of $\langle \cos(2Dp_i P_2(\theta_i)\tau) \rangle$ for 2τ > 6ms. A further check of this interpretation is provided by the time dependence of $E_1'(2\tau,\psi)$ for small angles ψ. As shown in fig.3 for $\psi \simeq \pi/6$ the amplitude $E_1'(2\tau,\psi)$ increases with time until $2\tau \simeq 5.5$ms. This behaviour is just that predicted by equation (4') if $\langle \cos(2Dp_i P_2(\theta_i)\tau) \rangle$ decreases with time and becomes negligible for times 2τ > 6ms. This time dependence does not however allow one to attribute a well defined value for the order parameters to the molecules (one should observe in this case characteristic beats) but rather a distribution of values with $p^* = \langle p_i^2 \rangle^{1/2} \simeq 0.1$, in agreement with the value infered from the line-width study. (A more detailed knowledge of the distribution cannot be obtained from data collected on a powdered sample). A possible origin of this distribution lies in the random repartition of ortho and para molecules, but slight differences between the different crystals which form the powder are not ruled out.

One can further note that the time constant $T_2(\psi)$ of the exponential decay regime of $E_1'(2\tau,\psi)$ which is reached for 2τ > 9ms increases as ψ decreases (compare fig.2a and fig.3). This fact (that we have studied in detail [14] in orientationally ordered solid H_2 and αN_2) is expected when the quenching effect discussed in §2 is effective. The small increase of $T_2^*(\pi/2)$ on cooling between 42.5 K and 39 K is also linked to this quenching which appears when orientational ordering sets in.

This pulsed NMR study therefore confirms that a residual orientational ordering is established in $\beta^{15}N_2$ on cooling between approximatively 42 K and 39 K.

5. Discussion

The existence of a residual orientational

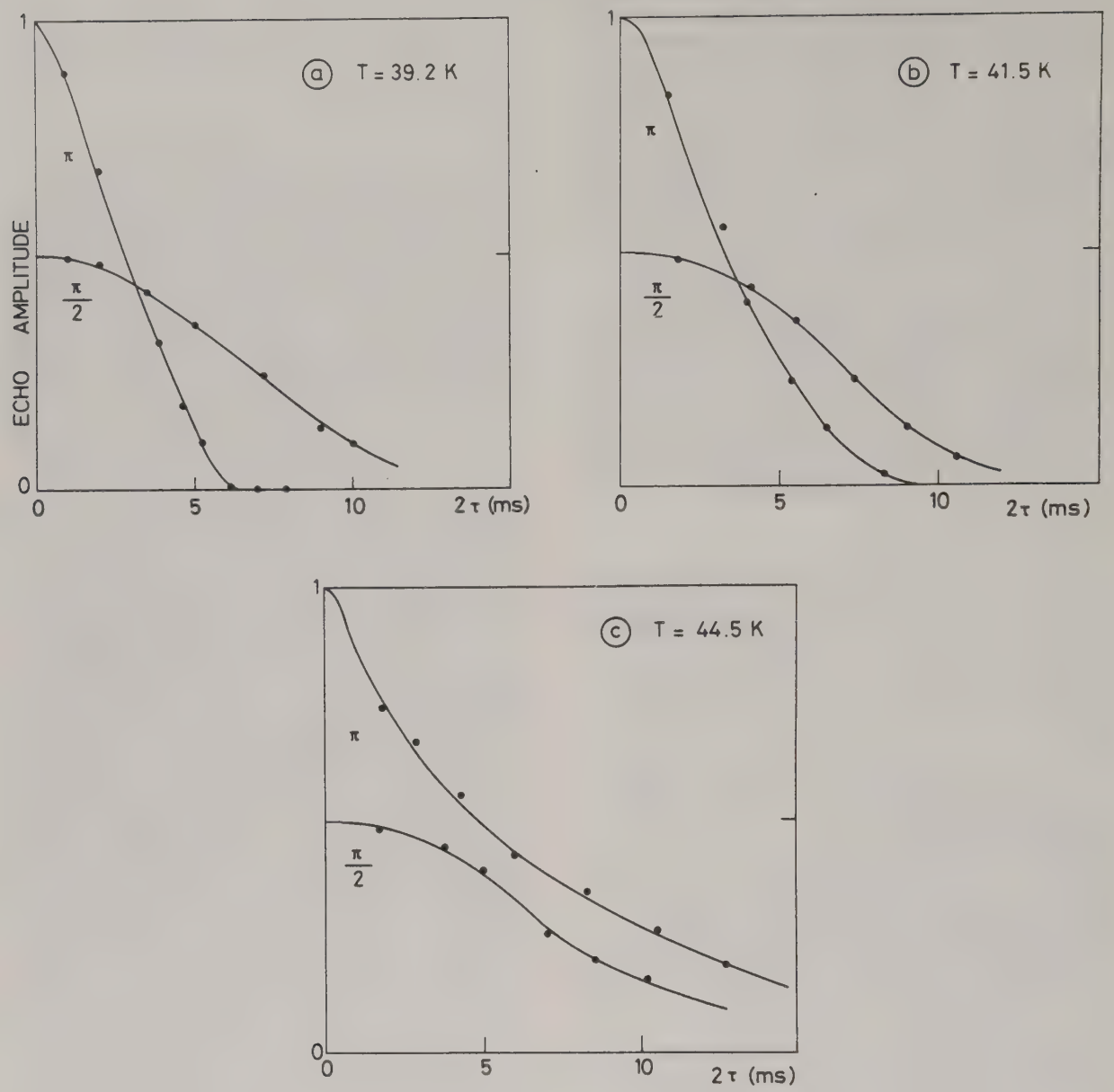

Fig.2. Comparison of the time dependence of the N.M.R. solid echo amplitudes $E'_1(2\tau, \psi = \frac{\pi}{2})$ and $E'_1(2\tau, \psi = \pi)$ at various temperatures a) T = 39.2 K
b) T = 41.5 K
c) T = 44.5 K

ordering much more developed in $\beta^{15}N_2$ than in $\beta^{14}N_2$ is of course consistent with the fact that the rotational heat capacities of both solids differ [12] . It may also be correlated with the different temperature dependences of their crystalline parameters.[12]

More precisely, we have observed a strong correlation with the difference in the behaviours of the anisotropy of the thermal expansion.

The difference $(\tau_c(T) - \tau_a(T))$ between the principal expansion coefficients versus T is shown for both solids in fig.4 : Whereas below 45 K it is positive, small and almost constant for $\beta^{14}N_2$, it is negative and decreases strongly as T decreases towards T_o for $\beta^{15}N_2$. Clearly the intramolecular dipolar line-width (dashed-line) becomes important in the same temperature range for which this anomaly arises. This correlated variation enforces the guess that the symmetry axes ζ_i coincides with the c axis of the

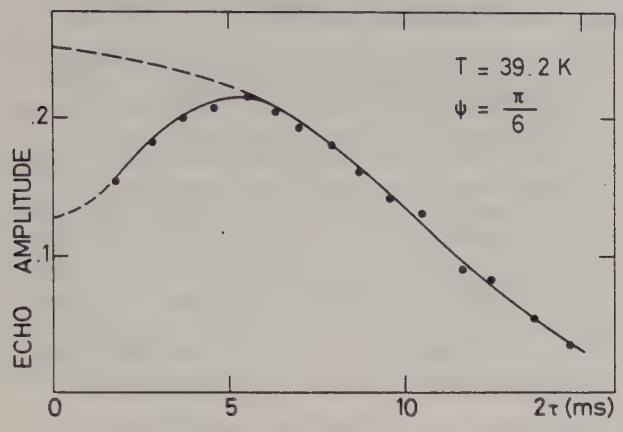

Fig.3. Time dependence of the echo amplitude $E_1'(2\tau, \psi = \frac{\pi}{6})$. The increase for $0 < 2\tau < 5.5$ ms is linked with the decrease of $\langle \cos(2D_{ij} P_2(\theta_{ij})\tau \rangle$ due to the presence of a residual orientational ordering.

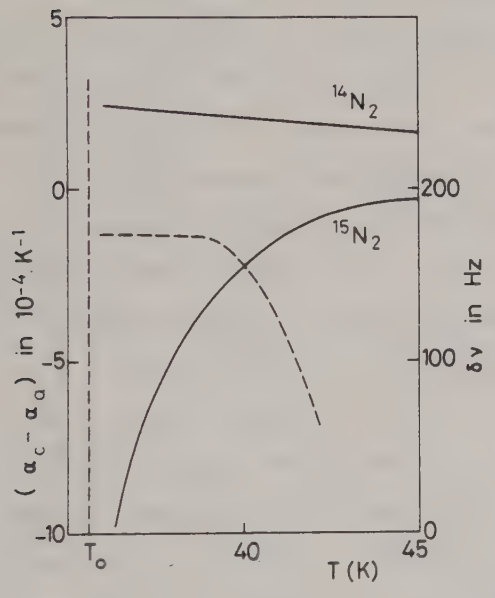

Fig.4. Temperature dependence of the anisotropy of the thermal expansion in both βN_2. The dashed line represents the intramolecular contribution to the line-width (right-hand scale).

crystal as in $\beta^{14}N_2$. Such correlations between orientational ordering and crystalline parameters, although currently admitted, have still received no theoretical backing.

The only existing theory of orientational ordering in $\beta^{14}N_2$ [19], based on a mean-field treatment of the Raich-Mills potential, has nevertheless shown that multipolar terms of higher order than quadrupolar ones are essential to explain any residual orientational ordering (but has failed to predict the value of the orientational order parameter). These multipolar terms, also necessary to account for the libronic frequencies and their Grüneisen coefficients in the different solid phases of $^{14}N_2$, are however still rather poorly known [1].

As a consequence of the greater mass of $^{15}N_2$ molecules their zero point motion has a smaller amplitude and it results in a reduction of the lattice parameters. This change does affect the anisotropic terms in the intermolecular potential more so for the higher order multipole terms than the quadrupolar terms. Nevertheless, these differences *alone* when considered in the framework of currently available theories do not explain the large difference in the orientational properties of the two solids. This difference provides therefore a severe test for any theory and can help in this way to determine the intermolecular potential more accurately. It is worth pointing out here that once given a Hamiltonian, the derivation of the orientational properties is still not an easy task (For example, the determination of the phase diagram of classical interacting quadrupoles on a s.c lattice is still an open problem [20]).

Conclusion

We have observed the presence of a residual orientational order in $\beta^{15}N_2$ just above the well-known order-disorder transition. A residual ordering has been previously reported for the common isotope $^{14}N_2$ but the NMR results presented here show unambigously that the orientational order in $\beta^{15}N_2$ is much more pronounced (by almost two orders of magnitude) than that observed in $\beta^{14}N_2$. This observation confirms the differences between the orientational properties of these solids previously inferred from the behaviour of their rotational heat capacities. The most striking comparison with other experimental studies comes however from the comparison of our results with the anomaly in the anisotropy of the thermal expansion in $\beta^{15}N_2$ in the same temperature range. Here again the effect is much more pronounced for the heavier isotope. These results therefore provide a serious challenge for a more complete theory of the β-phase of solid nitrogen.

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2. βN_2 : UN PROBLEME OUVERT

L'article précédent conclut à une différence entre les propriétés orientationnelles de $^{14}N_2$ et $^{15}N_2$. Nous détaillons ci-dessous les hypothèses sur lesquelles repose cette conclusion.

a) Notre interprétation de la RMN de $^{15}N_2$ en phase hexagonale suppose petits les effets des faibles interactions dipolaires intermoléculaires sur le comportement des échos solides. Dans la mesure où le problème des échos solides dans un système de spins 1 couplés par leurs interactions dipolaires (non réduites à leur partie diagonale) n'est pas résolu, l'étendue de validité de cette hypothèse est encore mal connue.

b) L'absence d'ordre orientationnel notable dans $\beta^{14}N_2$ est déduite de l'observation par RMN d'un gradient de champ électrique moyen extrêmement faible sur les noyaux ^{14}N et de l'hypothèse que ce dernier est essentiellement d'origine intramoléculaire. Un moyen d'obtenir une évaluation indépendante du paramètre d'ordre sans faire cette hypothèse consisterait à mesurer l'interaction dipolaire résiduelle entre les noyaux d'une molécule $^{14}N_2$: cela reviendrait à extraire d'une raie de quelques kHz de largeur (gradient de champ électrique résiduel vu par les noyaux ^{14}N) un terme dipolaire dont la contribution est tout au plus d'une centaine de Hz à la largeur totale. Ces deux types d'interactions étant cependant de natures différentes (interactions respectivement à un et deux noyaux), il est possible, théoriquement du moins, de détecter l'effet de la petite interaction dipolaire. Nous avons développé pour cela des séquences d'impulsions RF que l'on peut séparer en deux groupes :

i) des séquences produisant un écho par refocalisation de l'opérateur d'évolution des interactions quadrupolaires. On étudie alors la modification des échos induite par l'interaction dipolaire.

ii) des séquences qui ne fournissent pas d'écho pour l'interaction quadrupolaire seule mais qui en produisent un s'il existe une interaction dipolaire résiduelle. Ces séquences mettent en évidence dans la matrice densité nucléaire d'une molécule $^{14}N_2$($I=0,1,2$) la présence de termes $|\Delta m|>2$,

qui ne peuvent exister pour un noyau I=1 seul. L'utilisation d'un formalisme tensoriel est ici indispensable pour le calcul de l'opérateur d'évolution d'une séquence d'impulsions(voir figure D1).

Pour diverses raisons(existence des interactions intermoléculaires, imperfection des séquences d'impulsions, signal insuffisant ...) nous n'avons pu cependant tirer une conclusion sûre de nos expériences sur $^{14}N_2$: Le problème reste ouvert.

3. L'ORDRE ORIENTATIONNEL EN PHASE β POUR UN SYSTÈME DE QUADRUPOLES CLASSIQUES

Nous considérons des quadrupoles classiques aux noeuds d'un réseau hexagonal dont le rapport (c/a) peut différer de la valeur $\sqrt{8/3}$ du réseau compact. Les constantes d'interaction quadrupolaire diffèrent alors selon que la liaison est ou non dans un plan perpendiculaire à l'axe $\hat{c}$. La quadrupolarisation d'une molécule est à haute température axiale selon l'axe $\hat{c}$. On obtient au second ordre en 1/T (avec les notations du paragraphe B.III) :

$$\sigma_i = \sqrt{\frac{4\pi}{5}}\left(\frac{32}{63}\right)\beta^2 \sum_j \Gamma_{ij}^2 Y_{20}(\Omega_{ij})$$

expression qui s'annule pour un réseau compact si les constantes de couplage Γ_{ij} sont identiques.

Nous évaluons maintenant σ en supposant que $\Gamma_{ij} \propto 1/R^5$ comme pour une interaction quadrupolaire électrostatique. L'écart δ de (c/a) à la valeur $\sqrt{8/3}$ caractéristique du réseau compact introduit de légères modifications des distances intermoléculaires, des constantes de couplages et des angles spécifiant les liaisons. On obtient tous calculs faits au premier ordre en δ :

$$\sigma = \frac{32}{63}(\beta\Gamma)^2(-4\sqrt{6})\delta$$

soit

$$\sigma = -4.98\,(\beta\Gamma)^2\,\delta$$

Ce résultat se compare de façon curieuse avec la valeur mesurée par RMN dans $^{14}N_2$: hormis le signe, l'accord est excellent ! Il ne peut

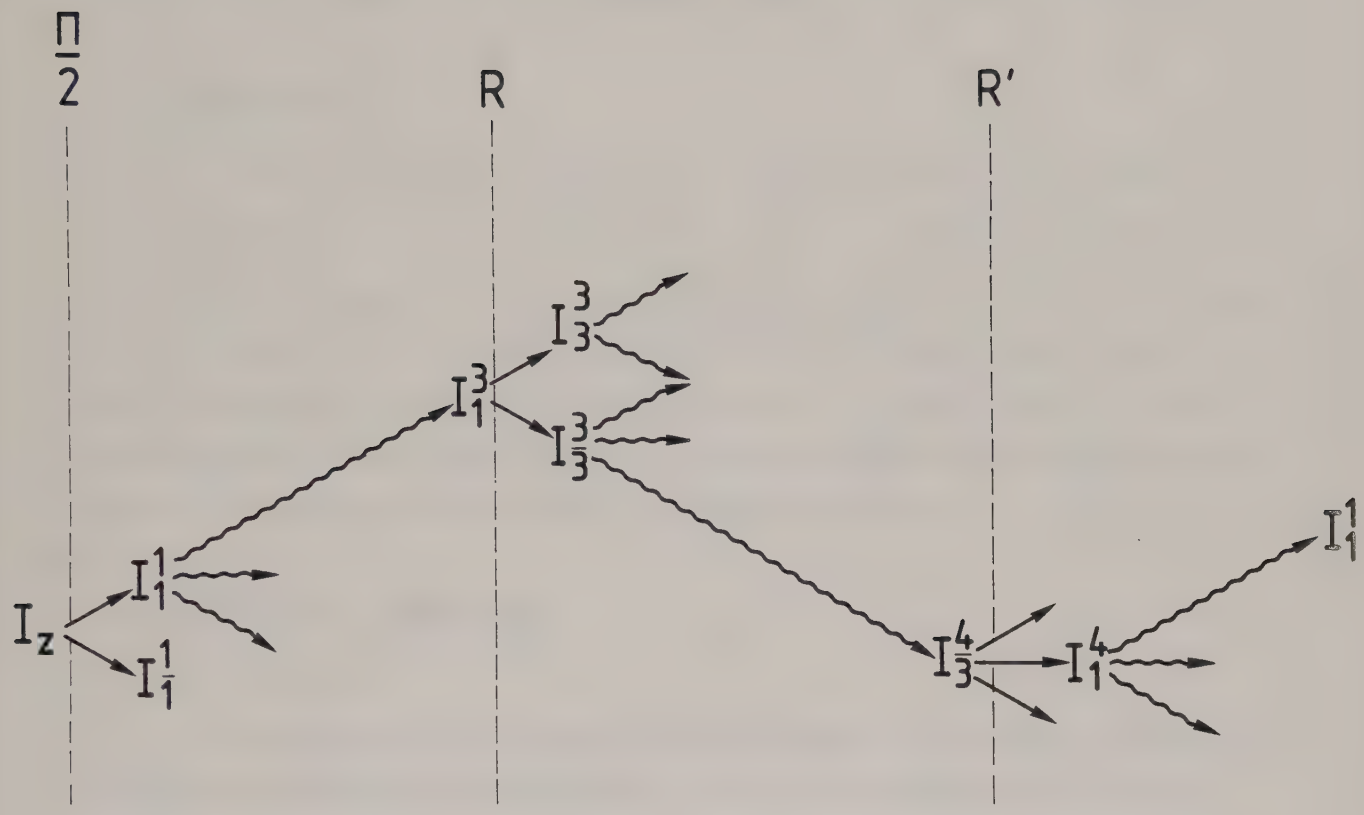


Figure D1 - Evolution de la matrice densité nucléaire d'une molécule $^{14}N_2$(I=2) au cours d'une séquence d'impulsions. Les opérateurs tensoriels I_Q^K évoluent au cours du temps (flèches ondulées) et lors des rotations (flèches droites). L'évolution temporelle introduit le mélange des divers rangs tensoriels K tout en conservant Q. Les rotations mélangent les I_Q^K à l'intérieur des multiplicités K. La bobine de RMN ne détecte que les termes vectoriels $I_{\pm 1}^1$. Un seul "chemin" conduisant à un tel terme a été complètement représenté.

expliquer par ailleurs l'existence d'un paramètre d'ordre résiduel important dans $\beta^{15}N_2$.

Il apparaît donc clairement que l'ordre orientationnel en phase hexagonale est dû aux termes non quadrupolaires du potentiel d'interaction.

III. LA RMN DE $^{15}N_2$ ORDONNE EN PHASE α

La phase α ayant été extensivement étudiée par RQN dans $^{14}N_2$, notre étude n'avait d'autre but que de mettre en oeuvre des méthodes RMN d'étude de l'ordre orientationnel. Nous donnons ici des résultats expérimentaux qui complètent ceux présentés dans les articles de la partie C.

1. LES SPECTRE CW

La figure D2 présente l'évolution du spectre RMN de $^{15}N_2$ solide à T=4.2K avec la fréquence de Larmor dans la plage 2-3.5MHz. On rend parfaitement compte des spectres (voir figure D3) en utilisant i) la valeur du paramètre d'ordre orientationnel mesuré dans $^{14}N_2$, p=0.863, ii) les valeurs de la constante dipolaire et du coefficient de déplacement chimique anisotrope déterminées par Ishol et Scott [IS77] et iii) la fonction de convolution tirée des résultats présentés dans la partie C pour tenir compte des interactions intermoléculaires.

2. LES METHODES D'IMPULSIONS

1 Impulsion

On observe après une impulsion RF le signal d'induction libre (voir figure D4) qui est la transformée de Fourier du spectre CW. En raison du déplacement chimique anisotrope, l'aimantation transverse ne relaxe pas dans le référentiel tournant en restant le long de l'axe X (voir figure D5). Cette circonstance rend délicats les réglages de la fréquence et de la phase de détection du signal, réglages qui ne peuvent être correctement effectuées qu'à l'aide de méthodes d'échos.

2 Impulsions : les échos solides

Nous complétons les résultats de la partie C en présentant les échos solides obtenus pour les séquences $(\frac{\pi}{2} - \tau - \pi_{\varphi=0})$ et $(\frac{\pi}{2} - \tau - \frac{\pi}{2}\ _{\varphi=0,\frac{\pi}{2}})$. Ces séquences fournissent directement les quantités suivantes (avec les notations du paragraphe C.III) :

$\langle \cos 2D_i\tau \rangle \widetilde{\mathcal{F}}_+(\pi,\tau)$ (voir figure D6)

$\langle e^{-2i\chi_i\tau} \rangle \widetilde{\mathcal{F}}_-(\frac{\pi}{2},\tau)$ (voir figure D7)

On note la séparation des effets de l'interaction dipolaire et du déplacement chimique anisotrope que l'on réalise ainsi. On atteint une précision de l'ordre de 1% dans la détermination du paramètre d'ordre orientationnel en utilisant les échos solides.

3 Impulsions : les échos stimulés

La figure D8 montre les échos que d'on observe dans $^{15}N_2$ ordonné après une séquence de trois impulsions. Parmi les trois échos possibles, l'écho stimulé dont l'instant de focalisation (τ après la 3ème impulsion) ne dépend pas du temps écoulé entre la 2ème et la 3ème impulsion joue un rôle à part : Il n'est pas amorti par les interactions dipolaires intermoléculaires dans la mesure où la diffusion spectrale dans la raie est bloquée. L'observation d'un écho stimulé après un temps d'attente t_w long (plusieurs secondes typiquement) prouve alors que les molécules ne tournent pas sur une échelle de temps de l'ordre de $D^2\tau^2t_w$ qui peut dépasser une centaine de secondes dans les conditions expérimentales de l'azote solide (cf §.C.III).

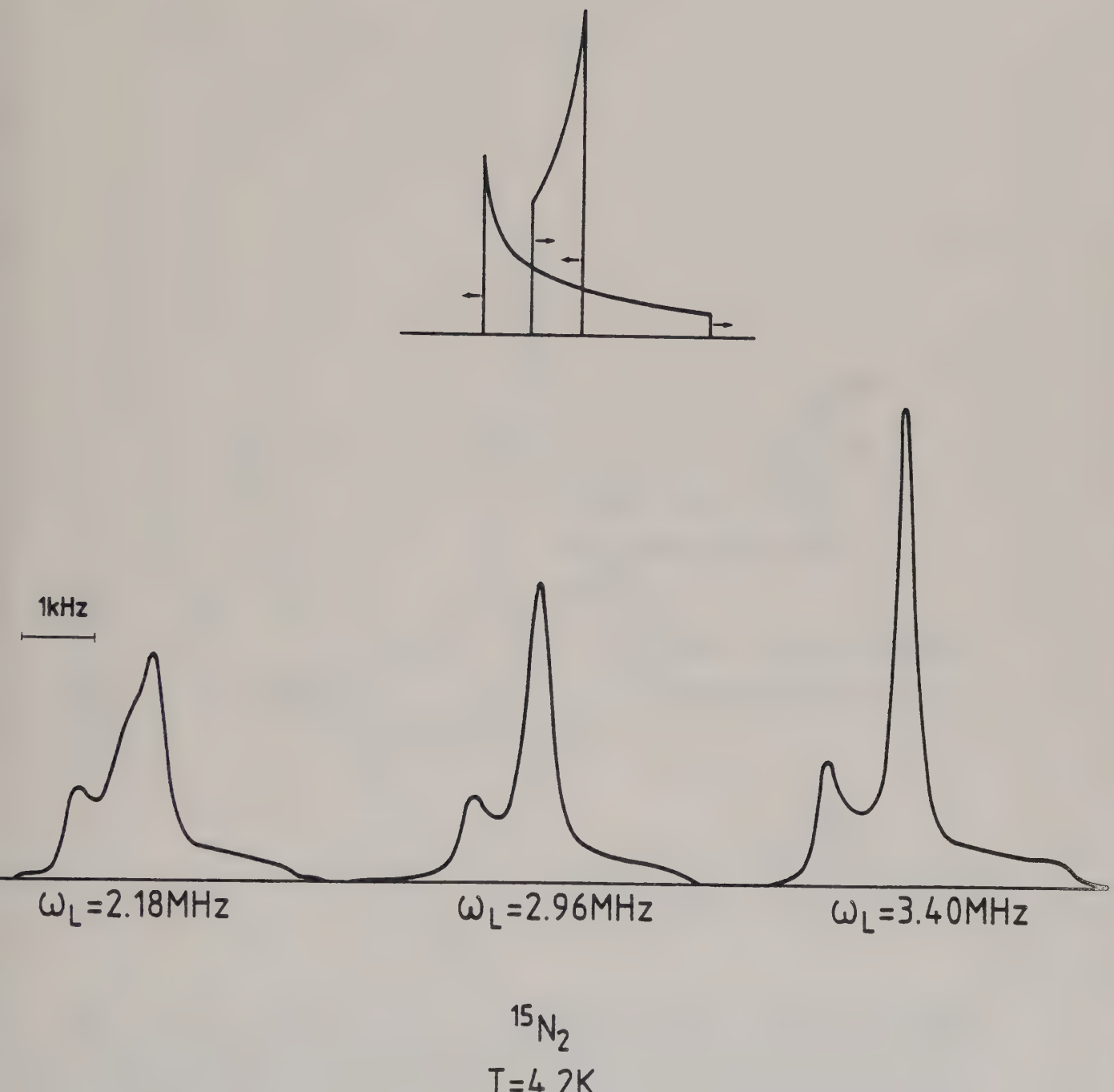


Figure D2 - Spectre RMN de $^{15}N_2$ solide (T=4.2K) à diverses fréquences de Larmor. Le déplacement chimique anisotrope (cf partie C) rend inégales les largeurs des deux "singulets" de Pake qui forment le spectre. Le schéma supérieur présente la façon dont se déforme le spectre lorsque la fréquence augmente.

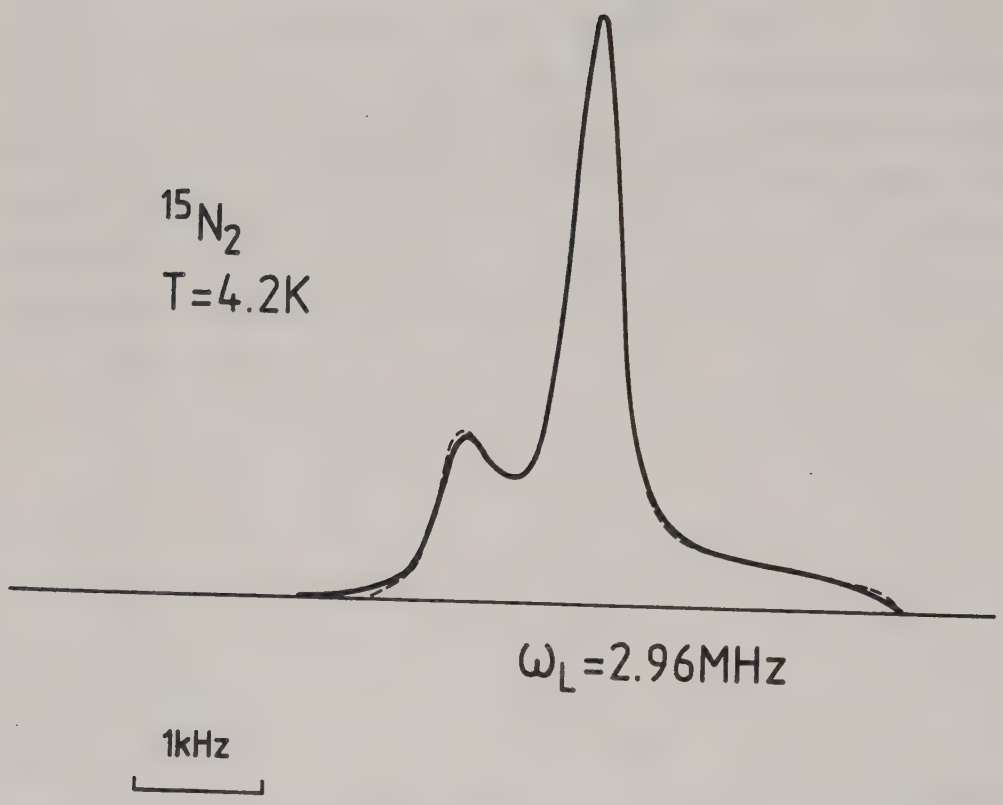


Figure D3 - Comparaison du spectre RMN de $^{15}N_2$ (T=4.2K) pour ω_L=2.96MHz à la forme de raie calculée. Le spectre expérimental est en trait plein. Le spectre calculé apparait en tireté lorsqu'il diffère du spectre expérimental. La fonction de convolution qui prend en compte les interactions intermoléculaires est une approximation analytique (produit d'une gaussienne par une lorentzienne) de la transformée de Fourier de la fonction d'amortissement des échos solides calculée dans la partie C. On a aussi tenu compte de l'élargissement dû à l'inhomogénéité du champ magnétique sur l'échantillon.

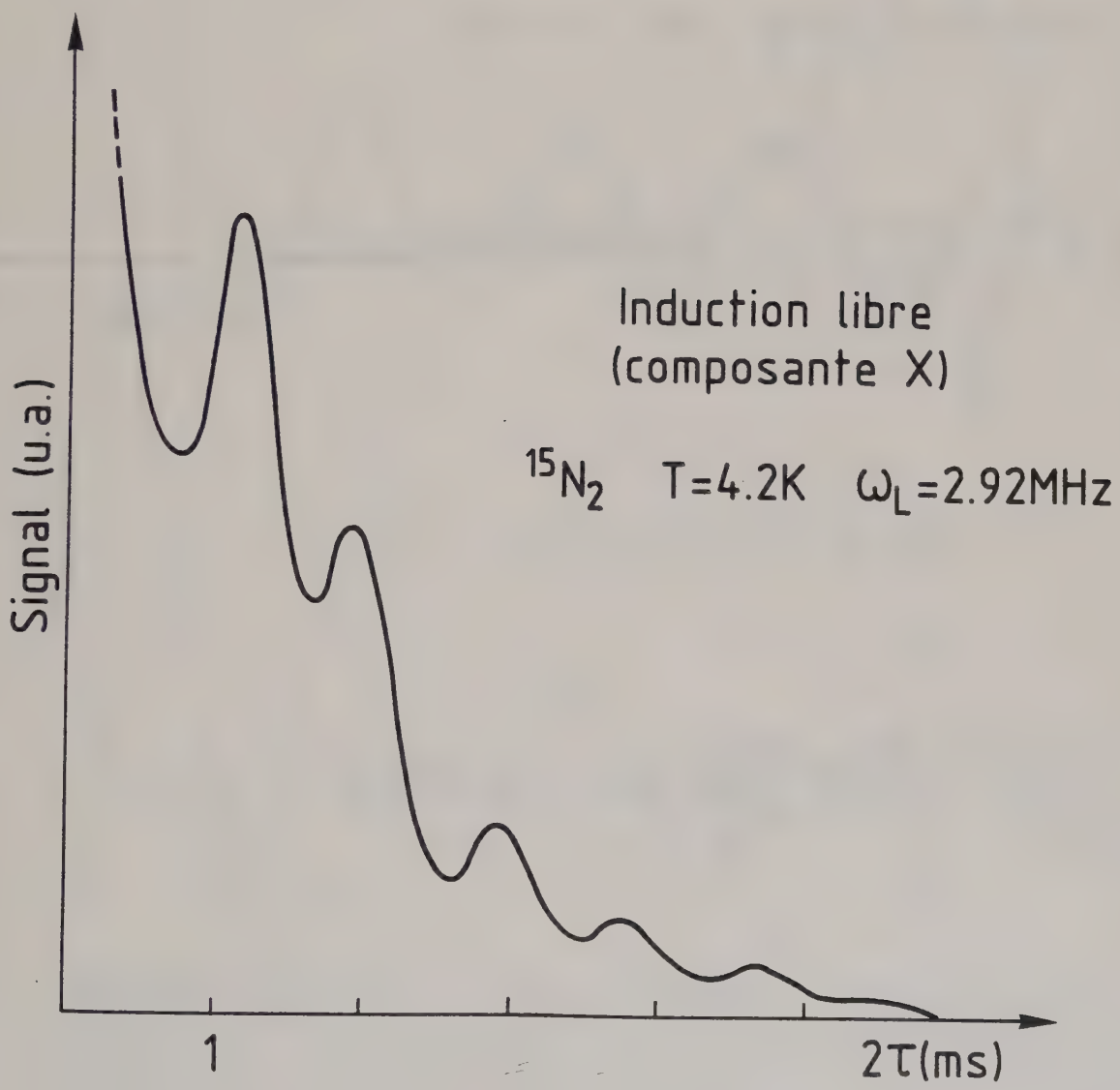


Figure D4 - Signal d'induction libre $I_X(t)$ observé dans $^{15}N_2$ solide à T=4.2K après une impulsion RF correspondant à une rotation de $\pi/2$ amenant l'aimantation le long de l'axe X dans le référentiel tournant.

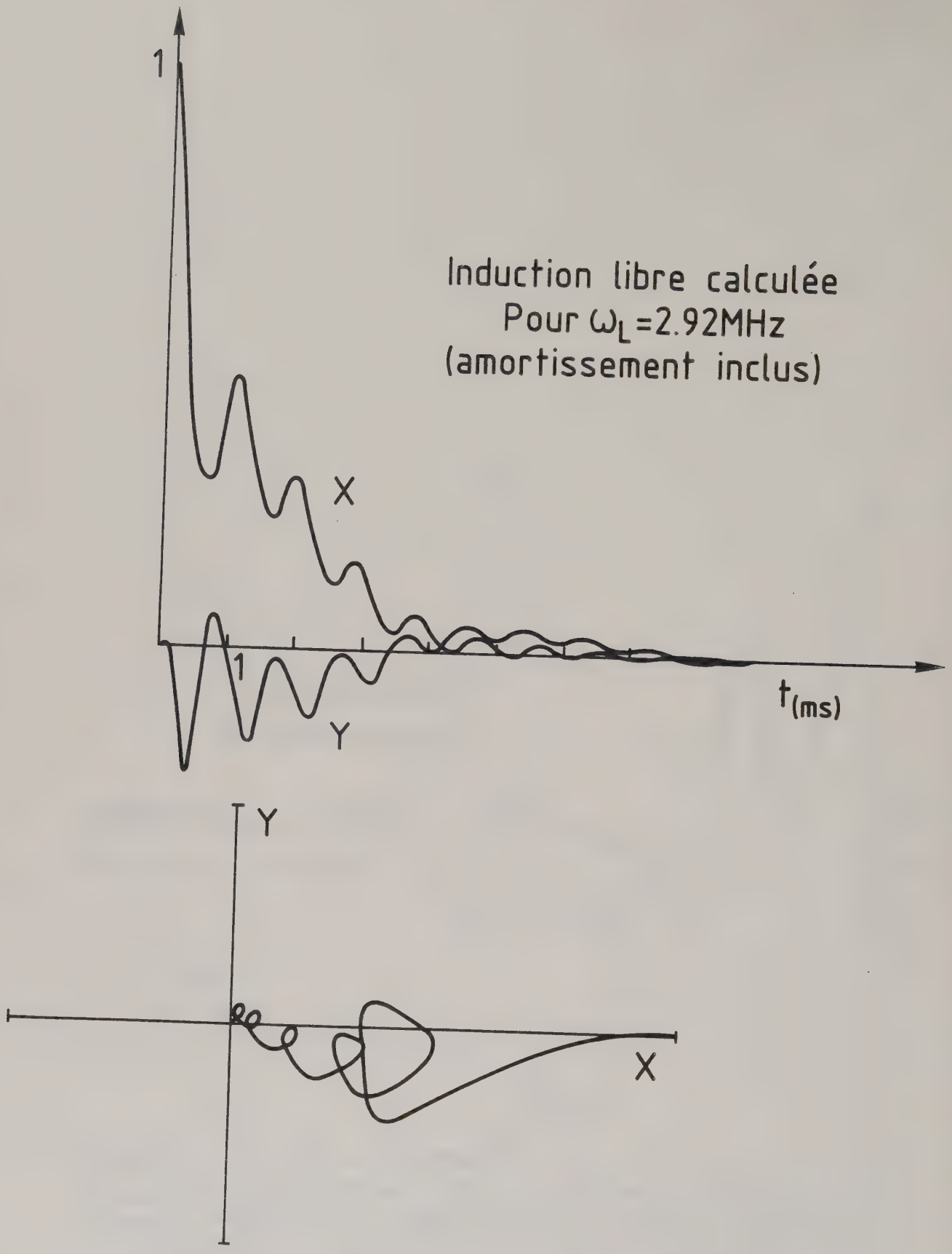


Figure D5 - Signal d'induction libre calculé pour $^{15}N_2$ solide à T=4.2K (ω_L=2.92MHz). En raison du déplacement chimique, la composante Y de l'aimantation transverse n'est pas nulle à tous les temps. La courbe suivie par l'extrêmité du vecteur représentant l'aimantation transverse dans le plan XY du référentiel tournant est donnée dans la partie inférieure. On observe effectivement les quatre premières boucles lorsque l'on utilise la fonction XY d'un analyseur multicanaux après enregistrement des composantes X et Y sur deux voies.

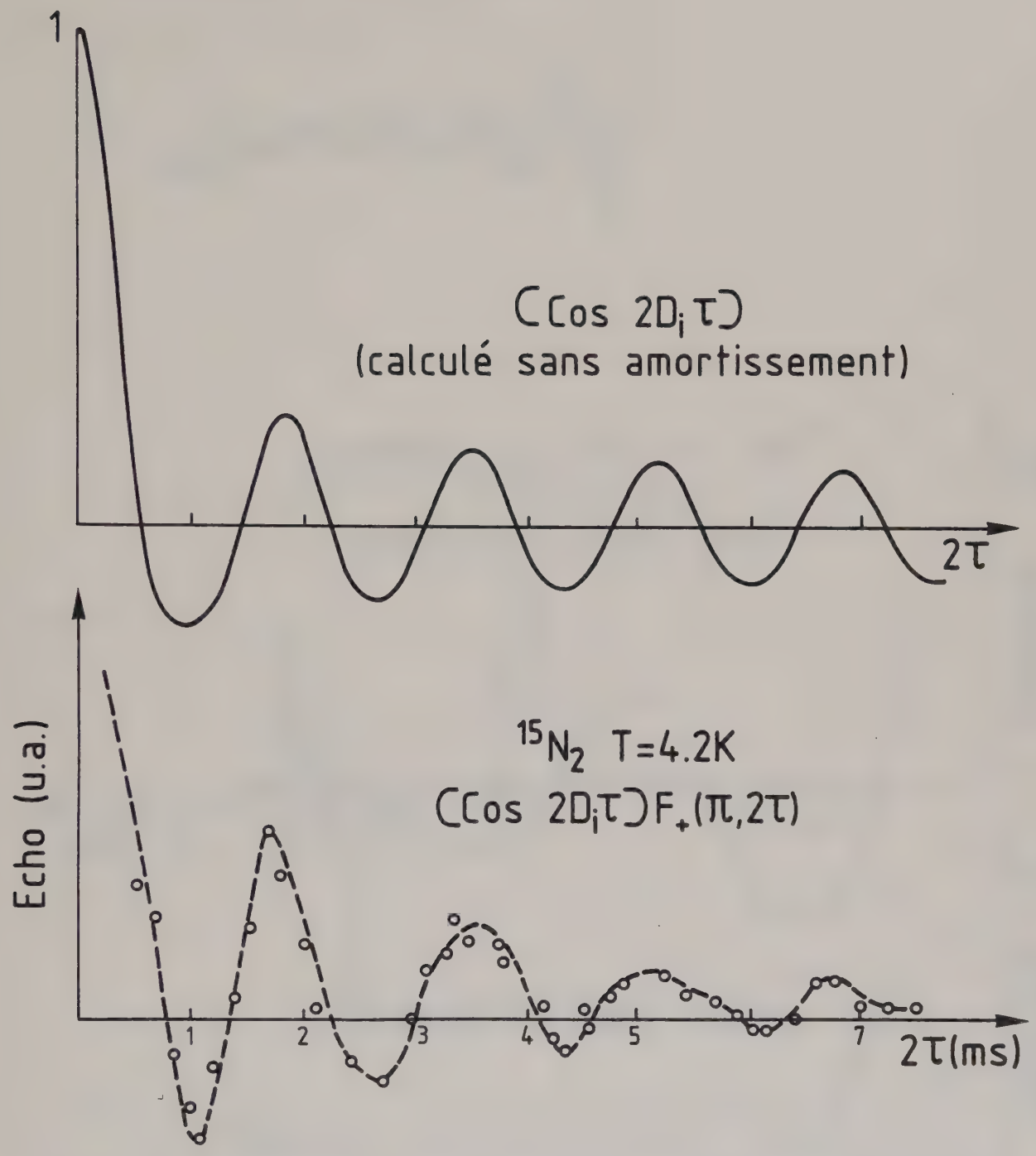
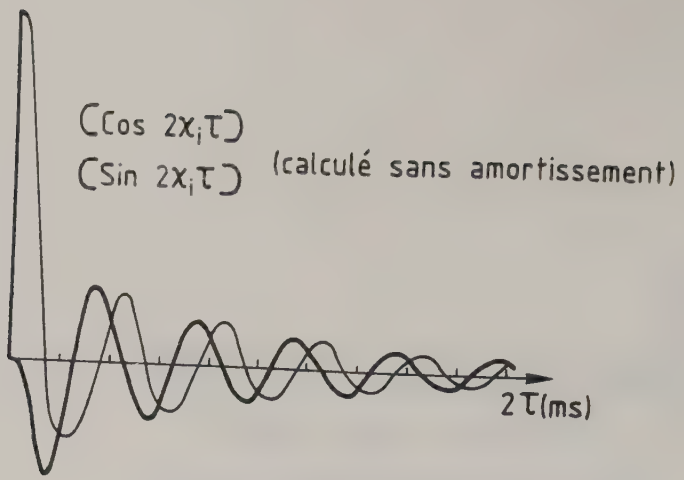


Figure D6 - Amplitude de l'écho solide suivant la séquence $(\frac{\pi}{2} - \tau - \pi_{\varphi=0})$ obtenu dans $^{15}N_2$ solide à T=4.2K. La partie supérieure représente la fonction $(\cos 2D_i\tau)$ que l'on obtiendrait en l'absence d'interactions dipolaires intermoléculaires. Ces interactions sont responsables de l'amortissement des battements (facteur F_+) et limitent ainsi la durée 2τ pour laquelle $(\cos 2D_i\tau)$ est observable. L'utilisation d'une séquence avec un angle de rotation ψ de la seconde impulsion petit permet d'augmenter cette fenêtre temporelle en profitant de la suppression de l'amortissement lorsque ψ tend vers 0 (cf.§.CIII).



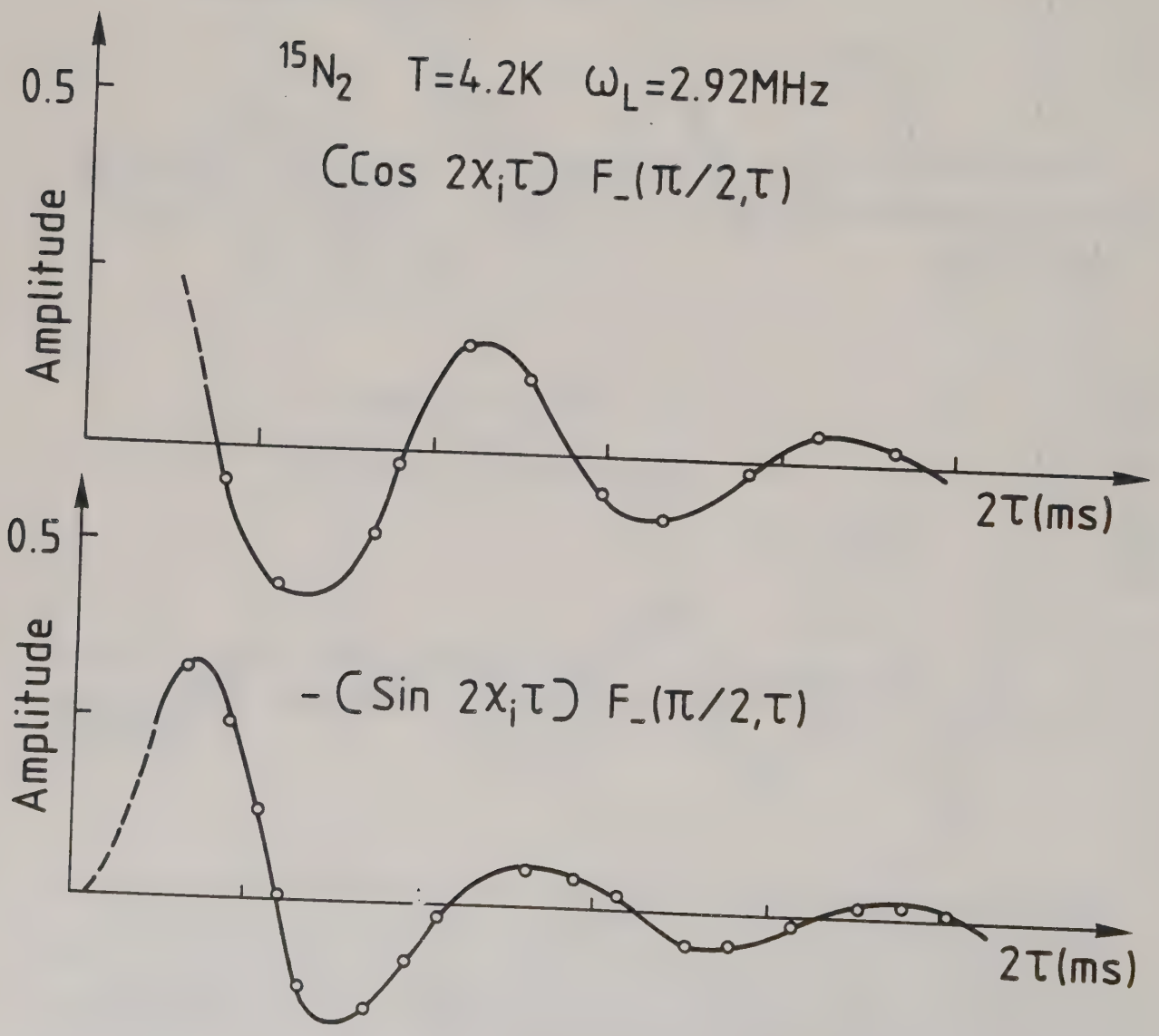


Figure D7 - Amplitudes $(\{^{\cos}_{-\sin} 2\chi_i\tau)\ F_-(\frac{\pi}{2},\tau)$ mesurées dans $^{15}N_2$ solide à T=4.2K ($\omega_L = 2.92$ MHz). Les fonctions $(\{^{\cos}_{\sin} 2\chi_i\tau)$ calculées sans amortissement sont portées dans la partie supérieure.

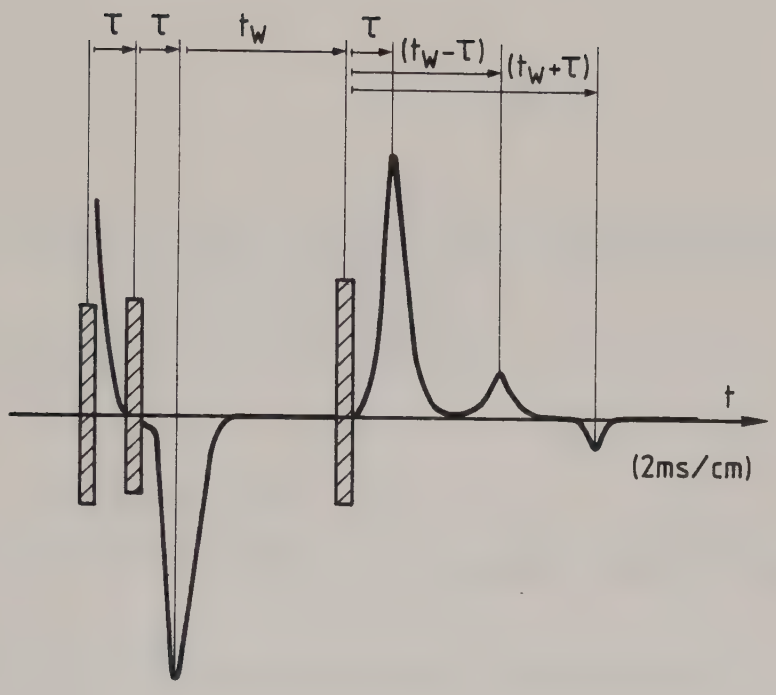


Figure D8 - Echos suivant la séquence d'impulsions $(\frac{\pi}{2}-\tau-\frac{\pi}{4}-t_w-\frac{\pi}{4})$. Un fort gradient de champ magnétique a été appliqué sur l'échantillon pour obtenir une séparation nette des différents échos.

PARTIE E : L'ORDRE ORIENTATIONNEL DANS LES MÉLANGES (N_2-Ar) EN PHASE HEXAGONALE

INTRODUCTION

I - MISE EN EVIDENCE D'UN VERRE ORIENTATIONNEL

II - SYNTHESE DES RESULTATS EXPERIMENTAUX

III - COMPARAISON AVEC D'AUTRES SYSTEMES "VITREUX"

INTRODUCTION

Nous donnons dans cette partie les résultats expérimentaux obtenus sur les mélanges azote-argon. Nous présentons ensuite un essai de synthèse de l'ensemble des propriétés de ce système connues à ce jour. Ces propriétés sont ensuite comparées à celles de quelques systèmes analogues.

I. MISE EN EVIDENCE D'UN VERRE ORIENTATIONNEL

1. ARTICLE

"Orientational ordering in a dilute system of interacting quadrupoles : (N_2-Ar) solid mixtures".

J. Physique — LETTRES **43** (1982) L-793 - L-799 15 NOVEMBRE **1982,** PAGE L-793

Classification
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Orientational ordering in a dilute system of classical interacting quadrupoles : (N_2-Ar) solid mixtures

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Résumé. — Nous présentons une étude RMN d'un mélange solide (N_2-Ar) pour $X_{N_2} = 0{,}67$. Dans ce système, les molécules d'azote peuvent être considérées comme des rotateurs classiques répartis au hasard sur un réseau hexagonal compact et couplés par des interactions anisotropes, de courte portée, du type quadrupôle-quadrupôle.
L'étude RMN de l'ordre orientationnel dans ce système, qui combine de façon originale la frustration et le désordre, montre qu'à basse température les molécules d'azote adoptent des orientations aléatoires essentiellement fixes dans le temps, tout mouvement de réorientation s'effectuant à des fréquences inférieures à 10^{-2} Hz. Ce régime, dit de verre orientationnel, s'installe progressivement lorsque la température diminue sans qu'une transition soit détectée. On pense cependant qu'il s'agit là d'un phénomène très coopératif.

Abstract. — We present an NMR study of a (N_2-Ar) solid mixture ($X_{N_2} = 0.67$) in which the N_2 molecules can be considered as almost classical rotators randomly distributed on an h.c.p. lattice. The orientational ordering of the molecules due to their short range highly anisotropic quadrupole-quadrupole interactions presents an original case study of the combined effects of frustration and disorder.
At low temperatures the NMR results show that the N_2 molecules adopt random frozen-in orientations for which any residual motion occurs at frequencies less than 10^{-2} Hz. This regime, called an orientational glass, grows continuously on cooling without any detectable transition but it is nevertheless believed to result from a highly cooperative phenomenon.

1. **Introduction.** — While ordinary glasses represent one of the oldest materials known to man, a comprehensive understanding of the formation of glasses has not yet been achieved. For this reason, interest has become focussed on conceptually simpler systems which are in many ways closely related to the general problem of glasses. The study of the so-called spin-glasses [1] has brought out the key role of the interplay between frustration and disorder in these compounds. Dilute systems of interacting quadrupoles, such as ortho-para H_2, para-ortho D_2, and N_2-Ar solid mixtures, which incorporate in a simple way both frustration and disorder, have therefore received a continuously growing interest. Frustration in these systems arises from the topological impossibility of ensuring the minimum possible energy for all pairs of neighbouring quadrupoles. This is so for any configuration of quadrupoles on any 3D lattice. In spite of this conflict, pure systems undergo orientational phase transitions to long range ordered phases which have rather complicated configurations but nevertheless achieve the best energy compromise. For example, on the f.c.c. lattice, one observes a four sublattice Pa3 structure [2, 3].

When some of the quadrupole bearing molecules are randomly replaced by spherical molecules or atoms, which just play the role of an inactive diluant from the orientational point of view,

the best energy compromise is not achieved for a long range ordered structure and the above transition no longer occurs. The study of solid ortho-para hydrogen [3-11] and deuterium [12] mixtures (in which the quadrupole bearing molecules, ortho H_2 and para D_2 are $J = 1$ quantum rotators) has shown that for quadrupole concentrations such that the lattice remains h.c.p. at all temperatures [13] ($X \lesssim 55\,\%$) a new regime referred to as a quadrupolar glass [4] is encountered at low temperatures.

This regime is characterized by (i) a broad non-uniform distribution of orientational order parameters (which measure to what extent the molecular orientations are localized); this distribution evolves smoothly with the temperature, (ii) a substantial slowing-down of the molecular reorientations [8, 10] on lowering the temperature, and (iii) a heat capacity varying linearly with the temperature [11]. An important unknown for these systems is however the importance of orientational quantum correlations between molecules. In order to understand the relevance of these quantum effects for the realization of a quadrupolar glass regime, we have studied N_2-Ar mixtures, in which the N_2 molecules can be considered as almost « classical » quadrupoles. We report in this letter an NMR investigation of the orientational ordering in this system for $X_{N_2} = 0.675$, that is in the concentration regime for which previous X-ray studies [14] have shown that (i) the lattice remains hexagonal at all temperatures and (ii) there is no phase transition towards a long range orientationally ordered phase, as confirmed by specific heat studies [15].

2. **NMR experiments.** — We have studied the NMR of a sample containing ^{15}N nuclei [16] ($I = 1/2$) instead of the NQR of the common isotope ^{14}N ($I = 1$) since the large quadrupolar coupling constant of the $^{14}N_2$ molecule would give rise to very large linewidths as soon as disorder is introduced in the system. Two molecular species of $^{15}N_2$ exist, ortho molecules ($I = 1$) and para molecules ($I = 0$). Since the difference in symmetry of the orbital functions plays no role at the temperatures being considered here, 75 % of the nitrogen molecules are ortho molecules whose nuclear magnetic resonance can be observed. It provides a powerful tool for studying their orientational state since the secular part of the intramolecular nuclear Hamiltonian H_n depends on the angle θ_i between the molecular axis $\hat{R}_i$ and the magnetic field applied along the $\hat{z}$ axis :

$$H_{n_i} = P_2(\theta_i)\,[-D(I_{iz}^2 - \tfrac{2}{3}) + \chi I_{iz}] \qquad (1)$$

where : $P_2(\theta_i) = \frac{1}{2}(3\cos^2\theta_i - 1)$, $D/2\pi = 1.38$ kHz is the intramolecular dipolar interaction and $\chi = (4 \times 10^{-4})\,\omega_0$ is the asymmetric chemical shift proportional to the Larmor frequency ω_0. In order to analyse the spectra, we shall assume that each molecule i undergoes a rapid rotational motion (compared to the relevant NMR frequencies D and χ) about a fixed symmetry axis $\hat{\zeta}_i$ (at angle α_i with the field). In this case, the NMR spectrum is determined by the statistical average of the $P_2(\theta_i)$ which obeys :

$$\langle P_2(\theta_i) \rangle = P_2(\alpha_i).x_i \qquad (2)$$

where the quadrupolarization x_i measures to what extent the molecule (i) is aligned along $\hat{\zeta}_i$:

$$x_i = \langle P_2(\gamma_i) \rangle \quad \text{with} \quad \gamma_i = (\hat{R}_i, \hat{\zeta}_i)\,. \qquad (3)$$

The NMR spectrum of the molecule (i) consists of two lines shifted from the Larmor frequency by :

$$\Delta\omega_i = P_2(\alpha_i).x_i(\pm D + \chi)\,. \qquad (4)$$

For a powder sample (uniform distribution of the α_i's), each value of x gives rise to an asymmetric Pake doublet (shown in the inset of figure 1) of width proportional to x. We have inferred

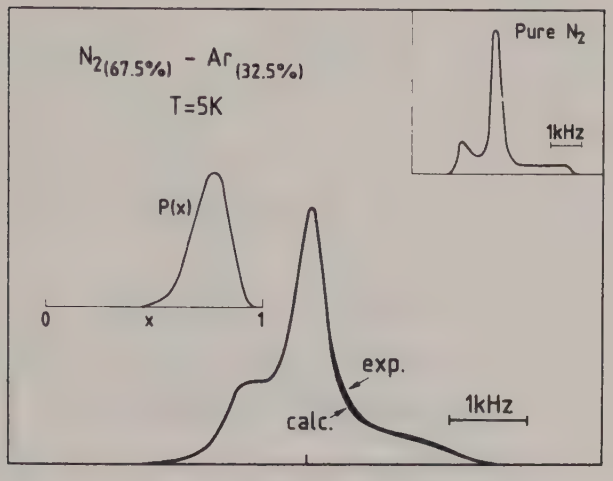

Fig. 1. — Comparison between the experimental NMR line shape recorded at a frequency of 2.9 MHz for a ($^{15}N_{2\ 67.5\%}$-$Ar_{32.5\%}$) sample at 5 K and the calculated one using the quadrupolarization distribution function $P(x)$ displayed. The line shape of pure $^{15}N_2$ (cubic phase, Pa3 structure) recorded under the same conditions is shown in the inset. It corresponds to the distribution $P(x) = \delta(x - 0.866)$.

the distribution function $P(x)$ for the x_i's from the NMR line shapes following recently developed procedures [5, 7] which have provided a satisfactory fit to the data as shown in figure 1. (Let us note here that the consideration of non-axial quadrupolarizations would not change our conclusions.)

The variation of the distribution $P(x)$ with the temperature is shown in figure 2. The most remarkable conclusion is that there is a continuous growth of $P(x)$ towards large quadrupolarizations as the temperature is reduced without any detectable discontinuity : the molecular orientations become progressively more and more localized on cooling from 20 K to 10 K, which corresponds to the temperature range for which an excess in the specific heat has been observed [15]. No further evolution is detected below 7 K : at these temperatures, the departure of the quadrupolarizations from the value $x = 1$ is a residual quantum effect. This evolution is qualitatively similar to the behaviour observed for ortho-para hydrogen mixtures [5, 7] and appears to be a general feature of dilute systems of interacting quadrupoles regardless of their quantum character.

We now turn to the evaluation of the time scale over which the picture of orientational states with fixed local axes $\hat{\zeta}_i$ can be considered as correct. We know that this time scale is greater than 10 ms since the line shapes are not in the intermediate motional narrowing regime. This limit is however too short to assess whether the molecular orientational states are well defined in time. In order to detect any residual motion, we have used pulse NMR methods specially conceived for that purpose and published elsewhere [17, 18]. The first method that we shall only briefly discuss consists of measuring the damping factor of the solid echo following two RF pulses separated by a time τ : since the damping of the solid echoes due to the dipolar intermolecular interactions is known precisely, an appreciable overdamping due to a possible slow motion of the axes $\hat{\zeta}_i$ (or to a possible slow time dependence of the quadrupolarizations x) can be detected if this evolution takes place in a time less than $(D^2\ \tau^3)$.

Our investigations of solid echoes in this system show conclusively that any slow motion in the system between 4 K and 20 K must have a characteristic time greater than 100 s. The second method allows one to probe the system on a longer time scale. It consists in measuring the damping of the stimulated echo following a sequence of three RF pulses, in which the waiting time t_w

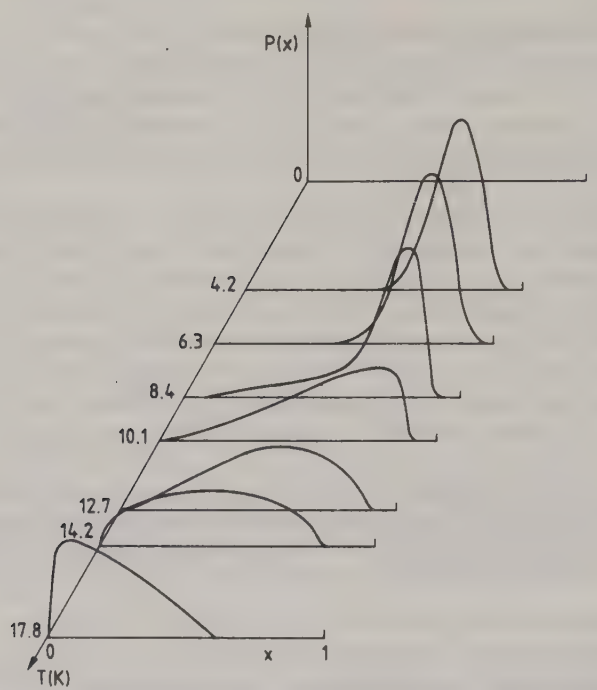

Fig. 2. — Evolution of the quadrupolarization distribution function $P(x)$ with the temperature as deduced from the analysis of the NMR line shapes.

before the third pulse is applied, is much greater than the time interval τ between the first and the second pulse (see Fig. 3). The two first pulses prepare the nuclear spins in a state of spin polarization and/or spin alignment which depends on the orientations of the local axes and of the values of the quadrupolarizations at that time. During the waiting time t_w, the nuclear spins come back toward thermal equilibrium at a very slow rate since the dipolar flip-flop transitions between nuclei of different molecules are almost completely forbidden. A time τ after the third pulse which interrogates the nuclear spin states, a stimulated echo is focussed only if the molecular orientational states have not changed too much during the waiting time t_w. In presence of a residual slow motion, the echo amplitude is affected by the following motional damping factor :

$$A(t_w) = \left\langle \frac{\cos(D + \chi)\,\Delta_i + \cos(D - \chi)\,\Delta_i}{2} \right\rangle \tag{5}$$

with :

$$\Delta_i = (\{ x_i P_2(\alpha_i) \}_{t=0} - \{ x_i P_2(\alpha_i) \}_{t=t_w})\,\tau\,.$$

For a slow motion of characteristic time t_m, both terms appearing in (5) are respectively appreciably damped as soon as t_m is shorter than a limit time $t_{L\pm}$ given by :

$$t_{L\pm} = (D \pm \chi)^2 \langle x^2 \rangle \tau^2 t_w\,. \tag{6}$$

We have carried out a complete calculation of the damping factor $A(t_w)$ in the case of a diffusive motion of the local axes $\hat{\zeta}_i$ which fully confirms this criterion. From the observed decay of the stimulated echoes one can infer a lower limit of 100 s for the characteristic time of any slow motion at all temperatures between 4 K and 20 K. The observed damping is probably mainly due to the

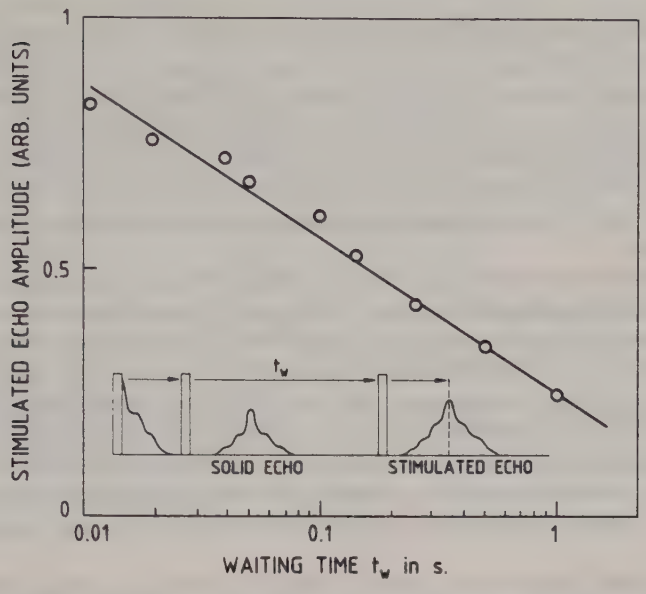

Fig. 3. — The observed decay of the stimulated echo following a three pulse RF sequence as a function of the waiting time t_w for a preparation time $\tau = 2.75$ ms at $T = 5$ K. The weakness of the damping allows one to place a lower limit of 100 s on the characteristic time of any residual slow motion.

residual spectral diffusion during the waiting time, since its time dependence (a logarithmic law on a wide time scale) is similar to what has been observed for the long range ordered phase of pure f.c.c. nitrogen (Pa3 structure), for which any residual rotational motion is excluded. Our basic hypothesis of well defined orientational states is therefore fully confirmed by these stimulated echoes experiments.

3. **An orientational glass regime.** — The principal result of this NMR study for solid (N_2-Ar) mixtures ($X_{N_2} = 0.675$) is the observation of a continuous growth of the quadrupolarizations of the molecules as the temperature is reduced without any detectable thermodynamic transition ([1]). We call this low temperature regime an orientational glass regime since the degrees of freedom which are frozen are those describing the orientation of a classical rod. To what extent one faces a collective phenomenon is clearly the most important question to be answered. At high temperatures, the small quadrupolarizations one observes result from pair correlations induced by the quadrupolar interactions between the N_2 molecules randomly distributed on the lattice. One would then expect [7] that on lowering the temperature, these correlations or similar ones involving only a few quadrupoles become stronger and that the system approaches its low temperature state continuously without any cooperative phenomenon taking place. This point of view seems in fact to be in contradiction to the results of recent Monte Carlo simulations of an assembly of interacting quadrupoles.

Previous work [19, 20] had already shown the presence of anomalously long evolution times in such a system. The MC experiments we have carried out [21] (random occupation ($X = 0.67$) of 96 and 216 sites on an h.c.p. lattice; up to 3×10^5 MCS (Monte Carlo Steps) per quadrupole at a given temperature) have indicated that : (i) on lowering the temperature, there is at first

([1]) Recent careful measurements of the specific heats of N_2-Ar mixtures [23] (for $X_{N_2} < 0.75$) also show a smooth temperature dependence without any hint of transitional behaviour.

a continuous growth of the local quadrupolarizations without appreciable modifications of the local axes $\hat{\zeta}_i$ until a cross-over towards a collective regime appears; (ii) this collective regime is characterized by correlated motions of the quadrupoles corresponding to jumps of the entire system between a few pockets in the configuration space, each pocket being associated with a ground state; (iii) on further lowering of the temperature, the system becomes trapped in a pocket. These results, although concerning a small system, show nevertheless that the onset of large quadrupolarizations in N_2-Ar mixtures is associated with collective rotational motions of at least 10^2 molecules.

Two types of collective behaviour have been identified in frustrated disordered systems, the so-called spin-glass and glass transitions. The evidence of a true transition in spin-glasses [22] (which is now supported by a large consensus [1]) arose from a careful examination of the magnetization and particularly of its field dependence. This type of experiment for quadrupole systems would correspond to measuring the response to an electrical field gradient and cannot be realized in a direct manner. In any case, the presence of quadrupolarizations at high temperatures would forbid measuring the analog of the zero field susceptibility. If one looks at dynamical properties, quadrupolar systems (at least ortho-para H_2 mixtures [10]) and spin-glasses display a very substantial slowing-down in a narrow temperature range; but evidence of a true transition cannot be inferred from it.

For conventional glasses, one does not observe a sharp transition in static properties but only a very rapid slowing-down. The glass state is characterized by strong time dependent effects (such as enthalpy and volume relaxation), and by the now well known two level systems. Such features have been alluded to in studies of quadrupolar systems [6, 10] but never studied in depth. Whether the orientational glass is a true equilibrium state (as now admitted for the low temperature state of spin-glasses), or a non-equilibrium state (as for conventional glasses) remains unknown, but experiments designed to answer this question are planned in different laboratories.

4. **Conclusion.** — Despite their very particular natures, the quadrupolar systems (N_2-Ar, ortho-para H_2 mixtures) form glass-like states (orientational and quadrupolar glasses) with properties very similar to those observed for ordinary glasses and spin-glasses. Since the only conceptual link between these very different systems is that they incorporate both frustration and disorder, the similarity in their behaviour supports the argument that the combination of these basic ingredients is essential for glass formation.

Note added in proof. — The results of recent neutron scattering experiments on N_2-Ar alloys by W. Press and colleagues are in qualitative agreement with the conclusions given here and we thank W. Press for communicating his results prior to publication (Press, W., Janik and Grimm, to be published in *Z. Phys.* (1982)).

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2. L'ANALYSE DES FORMES DE RAIE RMN

L'analyse des formes de raie RMN présentée dans l'article précédent repose sur l'hypothèse de quadrupolarisations axiales. Comme cela a été indiqué lors de la présentation de la méthode (partie C), les conclusions générales de l'analyse ne seraient pas modifiées par la considération de quadrupolarisations non axiales. La fonction de distribution du module de quadrupolarisation $\sqrt{\sigma^2+\eta^2}$ serait alors très voisine de P(x) : les deux distributions auraient les mêmes valeurs aux bornes de l'intervalle de définition [0,1] et le même second moment. Pour des quadrupoles classiques, l'hypothèse des quadrupolarisations axiales est de plus exacte dans la limite $T \to 0$. La figure E1 montre que l'on peut raisonnablement rendre compte des spectres à diverses températures dans le cadre de cette hypothèse.

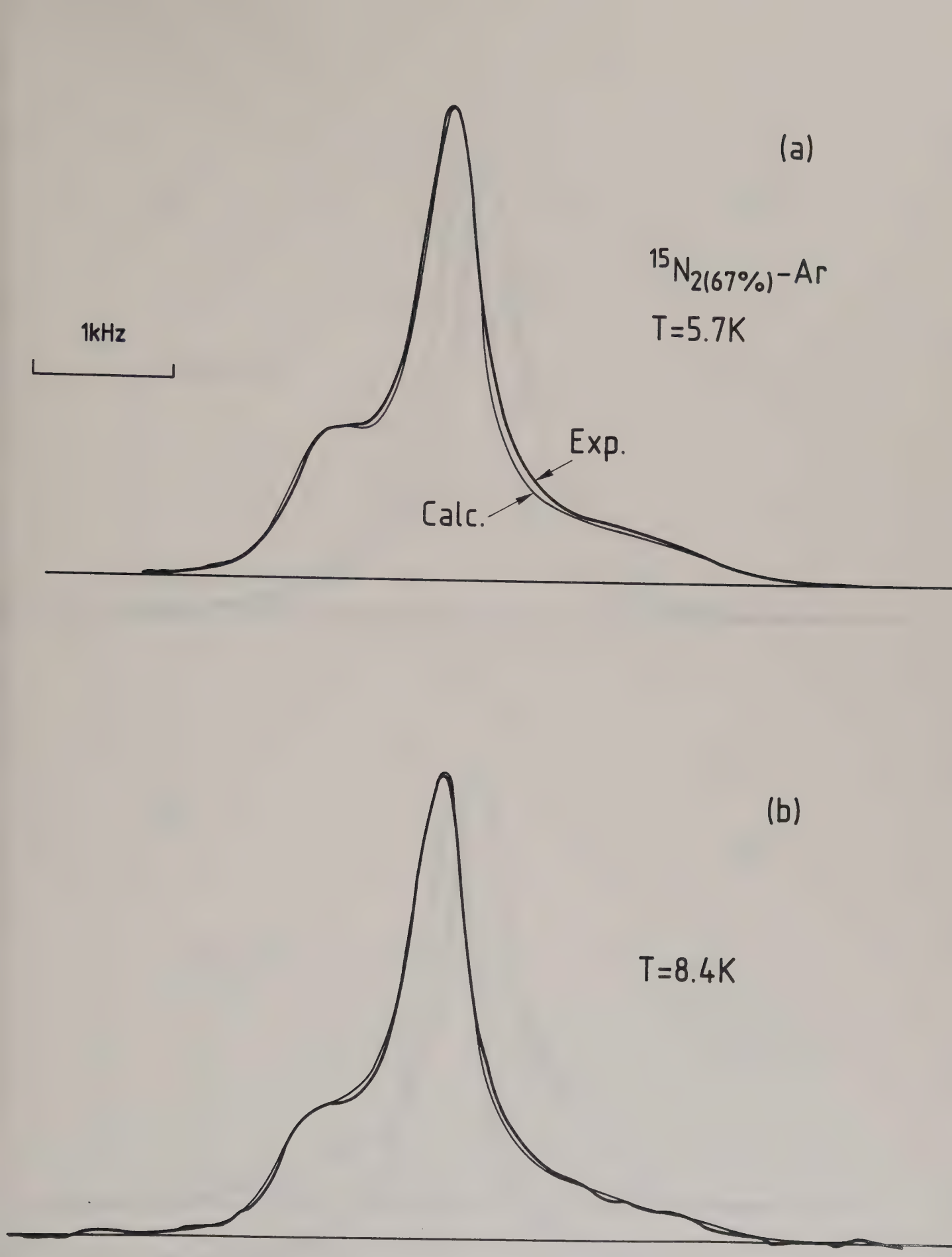
3. L'EVOLUTION DE LA DISTRIBUTION DES QUADRUPOLARISATIONS

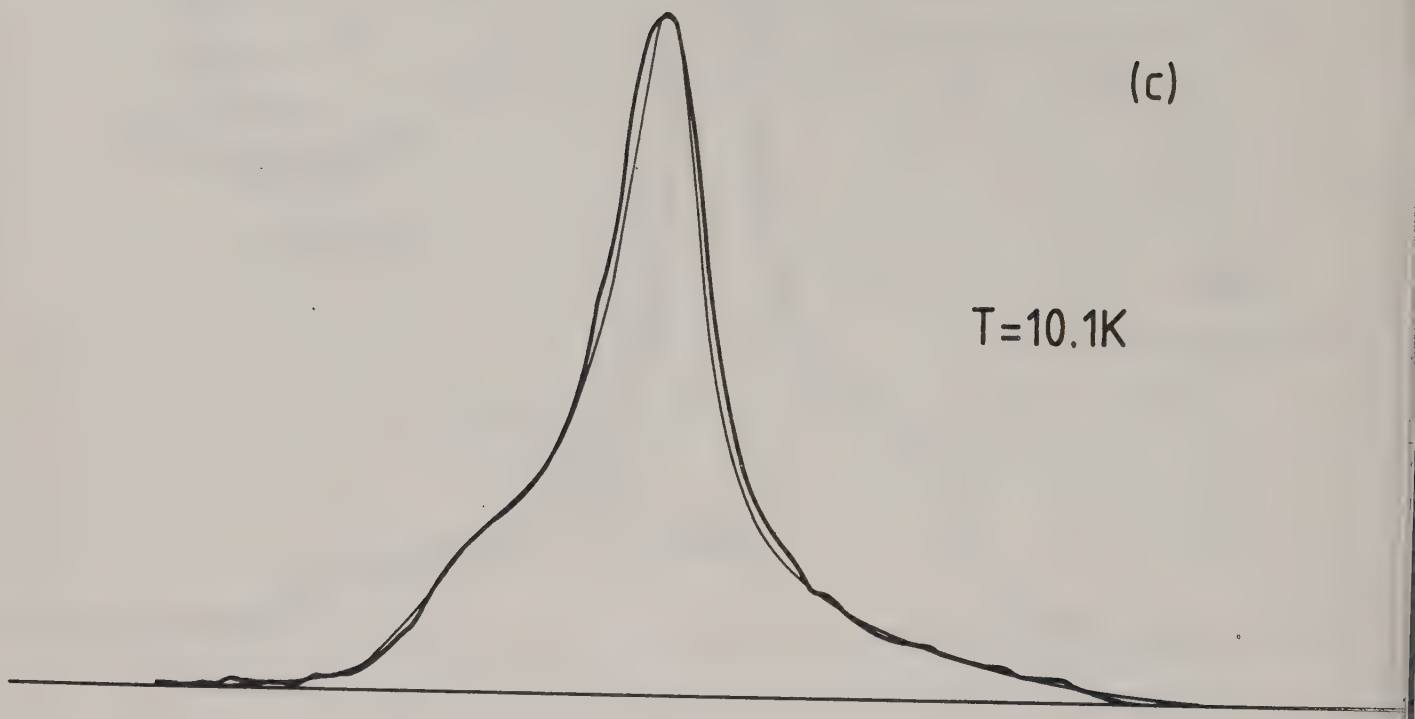
a) L'écart à la valeur x=1 des quadrupolarisations à basse température ($T \lesssim 7K$) est une conséquence de la "quanticité" rédisuelle des molécules d'azote. La largeur de la distribution de quadrupolarisation P(x) est par ailleurs beaucoup plus faible que celle observée dans les mélanges ortho-para d'hydrogène solide (cf partie C,§.II) : les corrélations quantiques entre molécules qui dans l'hydrogène solide sont responsables des faibles quadrupolarisations qu'adoptent à T=0K une partie des molécules jouent ici in rôle négligeable. Le verre orientationnel apparait à basse température comme proche d'un système de tiges classiques d'orientations aléatoires fixes dans le temps.

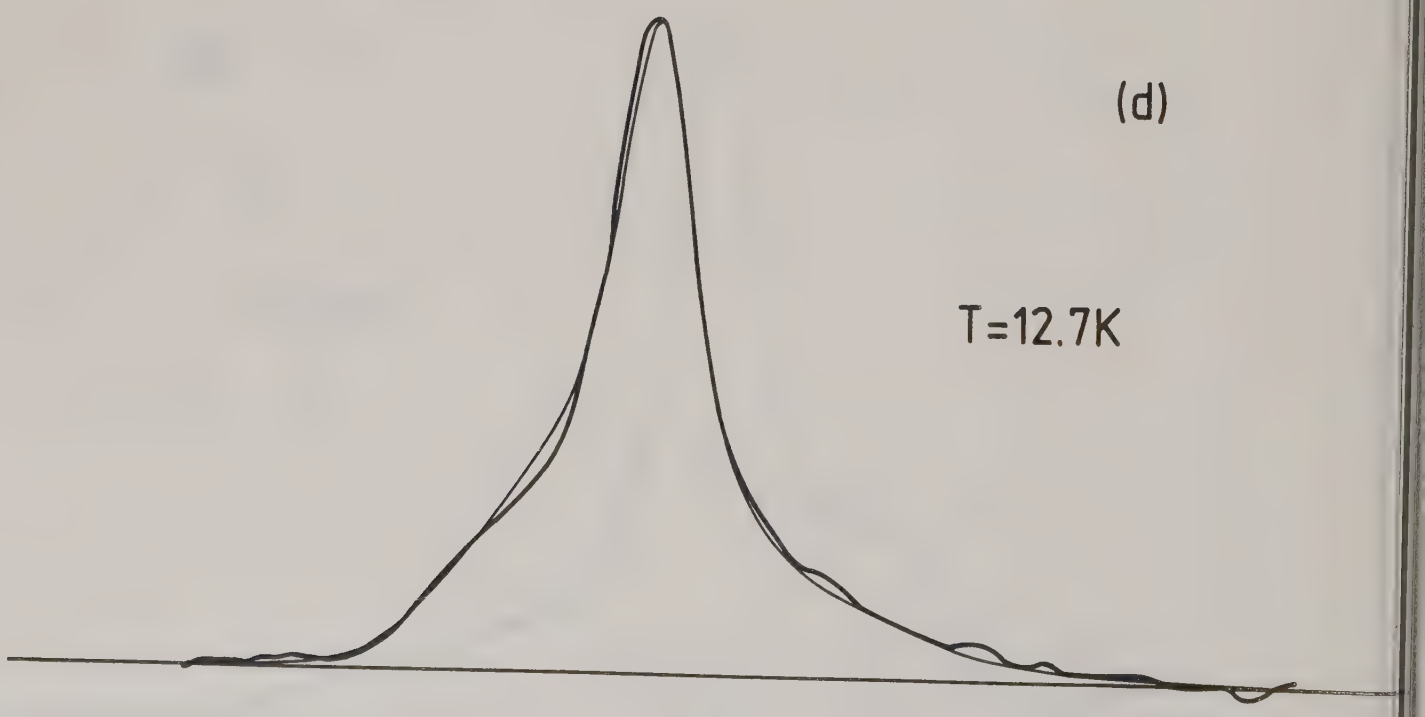
b) L'absence d'évolution de la distribution P(x) à basse température ($T \lesssim 7K$) est très significative, car un tel comportement se démarque nettement de celui d'un quadrupole classique dans un champ (cf partie B, §.III), qui ne présente pas de plateau à basse température.

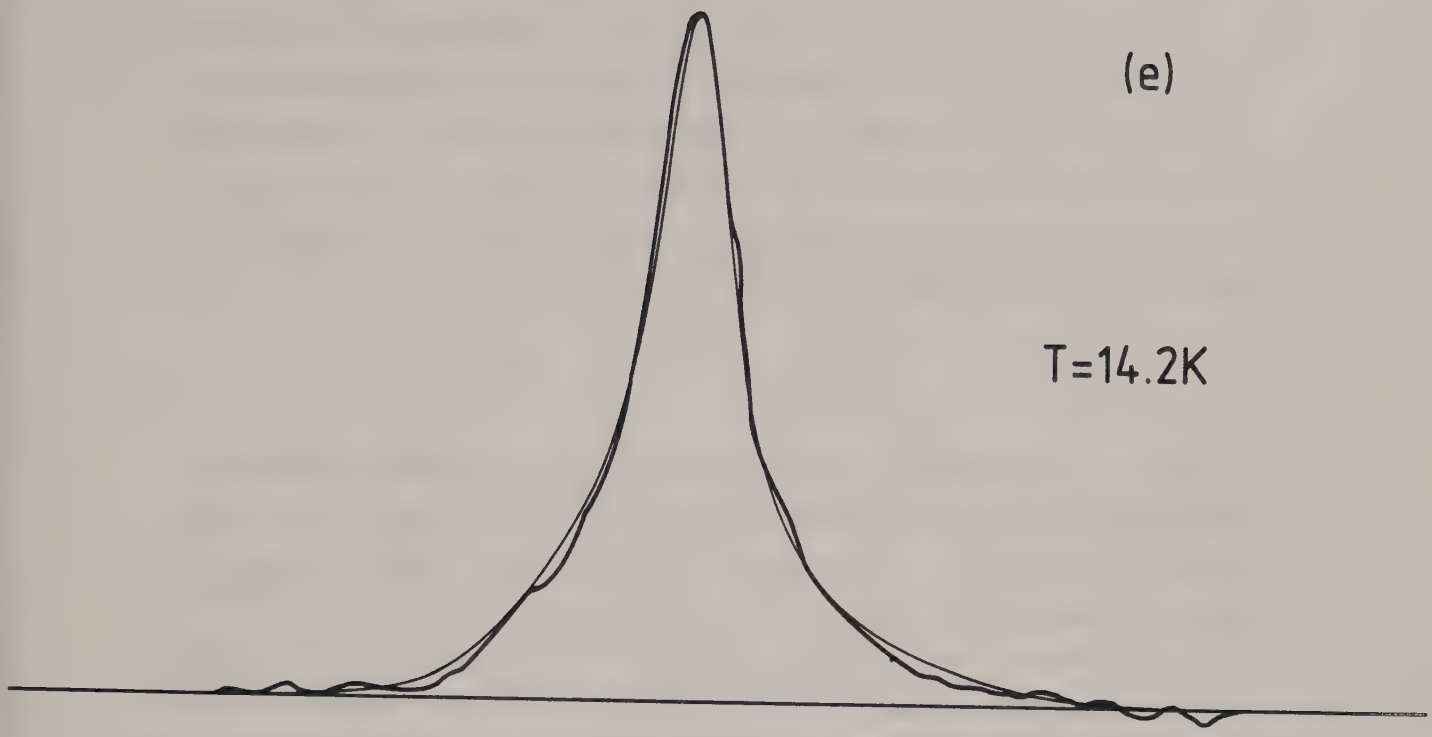
Nous avons essayé de préciser dans quelle mesure l'existence de cet arrêt à basse température de l'évolution des quadrupolarisations excluait toute interprétation en termes d'un modèle non collectif de quadrupoles placés dans des gradients de champ électrique aléatoires (champs cristallins éventuels).

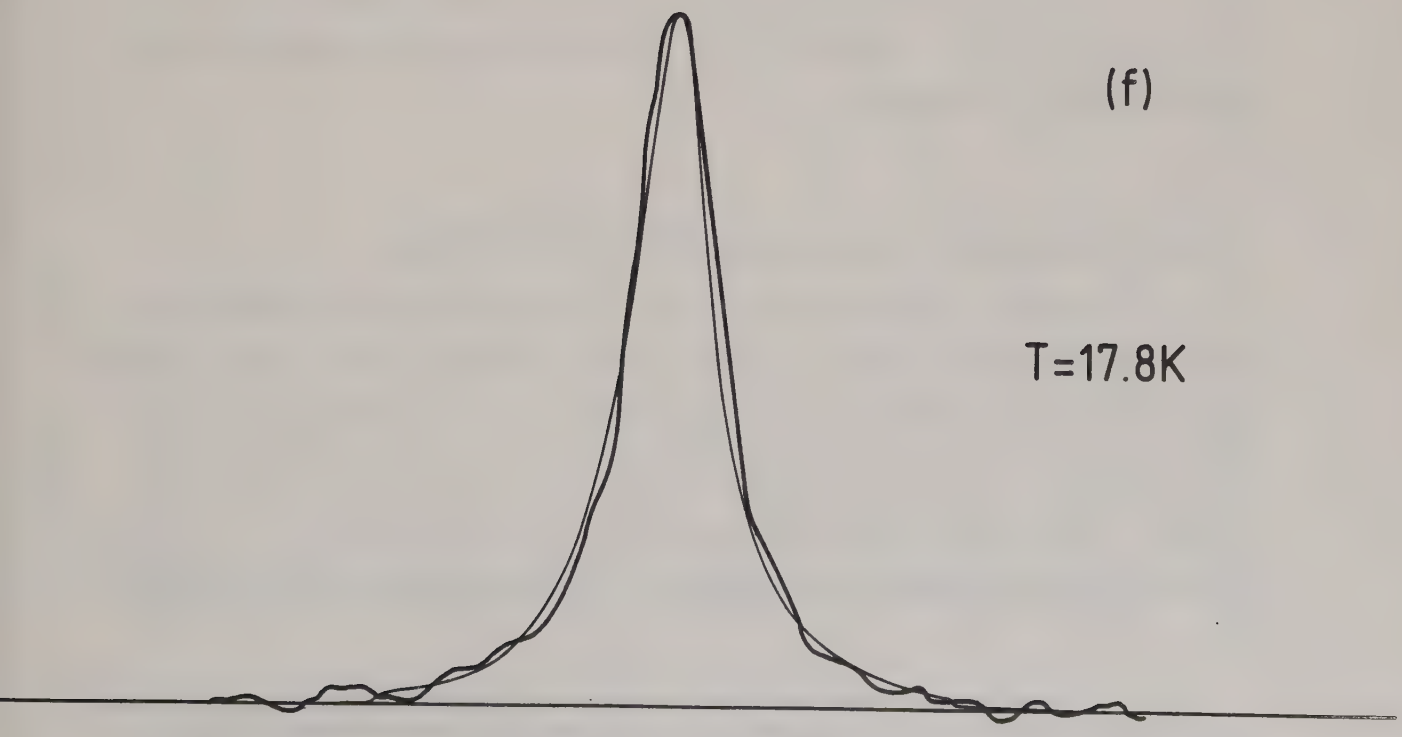
Figure E1 - Comparaison entre les spectres expérimentaux obtenus pour ($^{15}N_2$ - Ar) à X_{N_2} = 0.67 et les spectres calculés avec les distributions de quadrupolarisations présentées dans l'article précédent.


(a)
$^{15}N_{2(67\%)}$-Ar
T=5.7K
1kHz
Exp.
Calc.
(b)
T=8.4K


(c)
T=10.1K


(d)
T=12.7K


(e)
T=14.2K


(f)
T=17.8K

Dans le cadre d'un tel modèle, la distribution P(x) provient de la distribution des champs cristallins. Nous supposerons ici que ces champs sont tels que les quadrupolarisations des diverses molécules restent toujours ordonnées de la même façon à toutes les températures*. Il est alors aisé de déduire de l'évolution de P(x) l'évolution des quadrupolarisations individuelles : celles-ci sont tout simplement indicées par leur "numéro d'ordre" α, donné par

$$\alpha = \int_0^x P(u)\, du \qquad 0 \leq \alpha \leq 1 \ .$$

Le réseau de fonctions $x_\alpha(T)$ ainsi obtenues par résolution numérique de ces équations pour les distributions P(x) déterminées expérimentalement est indiqué sur la figure E2. Ces fonctions $x_\alpha(T)$ présentent un plateau à basse température, et ne peuvent pas s'interpréter en termes de champs cristallins constants agissant sur des quadrupoles classiques. (Il faut cependant noter qu'un tel plateau existe pour des quadrupoles quantiques dans un champ cristallin, mais que sa largeur attendue pour une molécule d'azote est inférieure à celle observée).

Comme les données du problème le laissaient prévoir (cf partie B), ce ne sont donc probablement pas les champs cristallins éventuels, mais bien les interactions quadrupolaires, qui sont responsables du gel des quadrupoles que l'on observe à basse température dans les mélanges azote-argon en phase hexagonale.

4. LA DIFFUSION SPECTRALE DANS LE VERRE ORIENTATIONNEL

La diffusion spectrale au sein de la raie RMN est extrêmement lente dans le verre orientationnel, ce qui permet d'observer des échos stimulés après un temps d'attente t_w pouvant atteindre plusieurs secondes. Nous avons ainsi pu obtenir une borne inférieure de l'ordre de 100s au temps caractéristique de tout mouvement lent de rotation des molécules dans le verre orientationnel entre 4K et 20K (voir l'article précédent et certains résultats complémentaires présentés dans la figure E3). Dans l'hypothèse

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*Cette hypothèse est exacte si les champs cristallins sont axiaux. Nous pensons que seule la clarté de l'analyse (et non sa conclusion) en dépend.

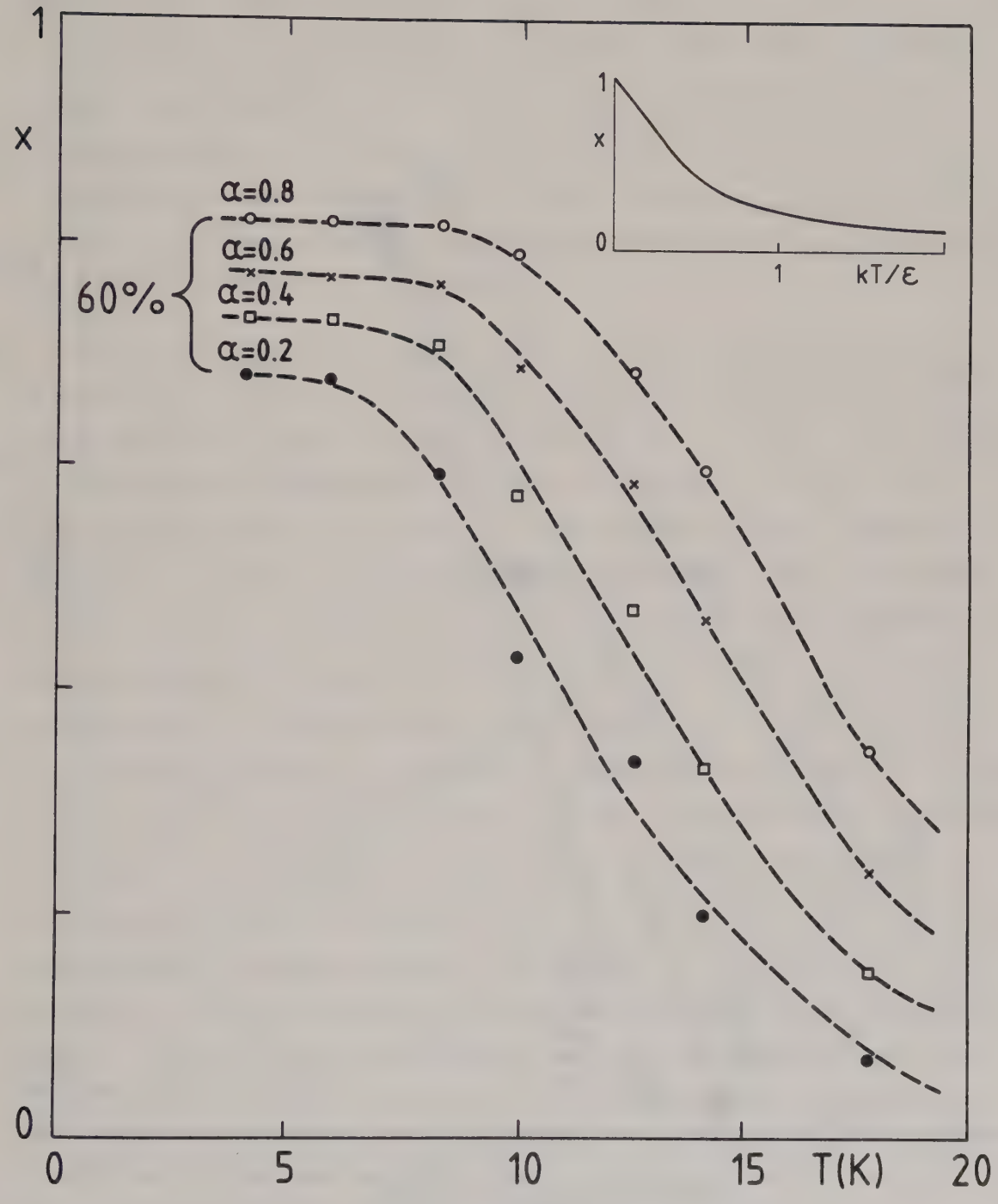


Figure E2 - Evolution des quadrupolarisations individuelles $x_\alpha(T)$ dans l'hypothèse où celles-ci se présentent à toute température dans le même ordre. La quadrupolarisation d'une molécule-tige *classique* dans un gradient de champ électrique (cf.§.BIII, cas $\varepsilon > 0$) est donnée en encart.

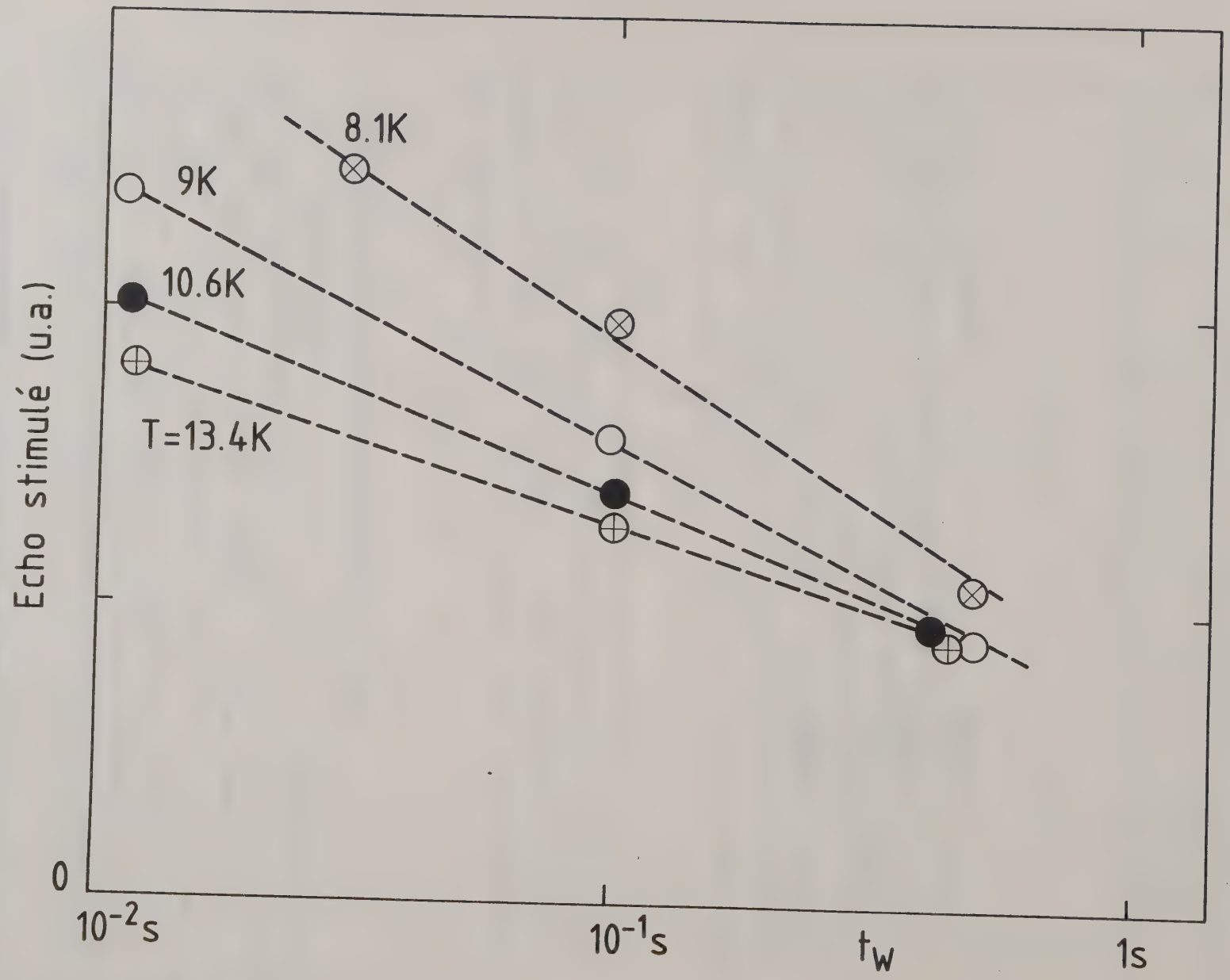


Figure E3 - Décroissance des échos stimulés observée dans N_2-Ar ($X_{N_2} = 0.67$) à diverses températures. Le temps de préparation est de 3.5ms.

où l'amortissement résiduel des échos stimulés est entièrement dû à la diffusion spectrale, il constitue une source d'informations sur les corrélations locales qu'entretiennent entre elles les molécules voisines : les flip-flop induits par les interactions intermoléculaires qui sont responsables de la diffusion spectrale s'effectuent en effet principalement entre molécules voisines (afin qu'il existe un couplage dipolaire intermoléculaire) et partageant une fréquence commune dans le spectre (afin que la différence d'énergie intramoléculaire ne soit pas plus grande que ce couplage). En l'absence de théorie satisfaisante de la diffusion spectrale dans une raie inhomogène, le décryptage de l'amortissement des échos stimulés pour en tirer des informations sur les corrélations orientationnelles entre molécules dans le verre orientationnel ne semble cependant guère possible.

Le seul fait expérimental significatif est la différence de comportement de la diffusion spectrale dans le verre orientationnel et dans la phase ordonnée à longue distance de l'azote pur : le temps t_o caractérisant la décroissance logarithmique de l'écho stimulé est plus faible dans le verre orientationnel et ne montre pas une dépendance aussi importante vis à vis du temps de préparation τ (voir figure E4). Cette différence prouve bien que les molécules d'un cristallite ne sont pas ordonnées selon la structure Pa3 dans le verre orientationnel, comme l'indiquent les expériences de diffusion de neutrons. Le sens d'évolution du temps caractéristique t_o en fonction du temps d'évolution τ peut par ailleurs se comprendre aisément : La séquence de préparation crée dans la raie une température Zeeman inhomogène donnée par une loi cosinusoïdale de période (en fréquence) inversement proportionnelle au temps de préparation (cf §.CIII) ; La diffusion spectrale s'effectuant alors d'autant plus vite que les molécules voisines en fréquence ont des températures Zeeman qui diffèrent de façon importante, il est logique que le temps caractéristique t_o soit une fonction fortement décroissante du temps de préparation τ. Il est aussi compréhensible que cette décroissance soit moins marquée pour les grandes valeurs de τ lorsque la période (en fréquence) de la température Zeeman après la séquence de préparation devient de l'ordre de la fréquence caractéristique des interactions intermoléculaires.

L'observation d'une relaxation en logarithme du temps reste plus mystérieuse. Nous avons effectué la simulation numérique de l'amortissement

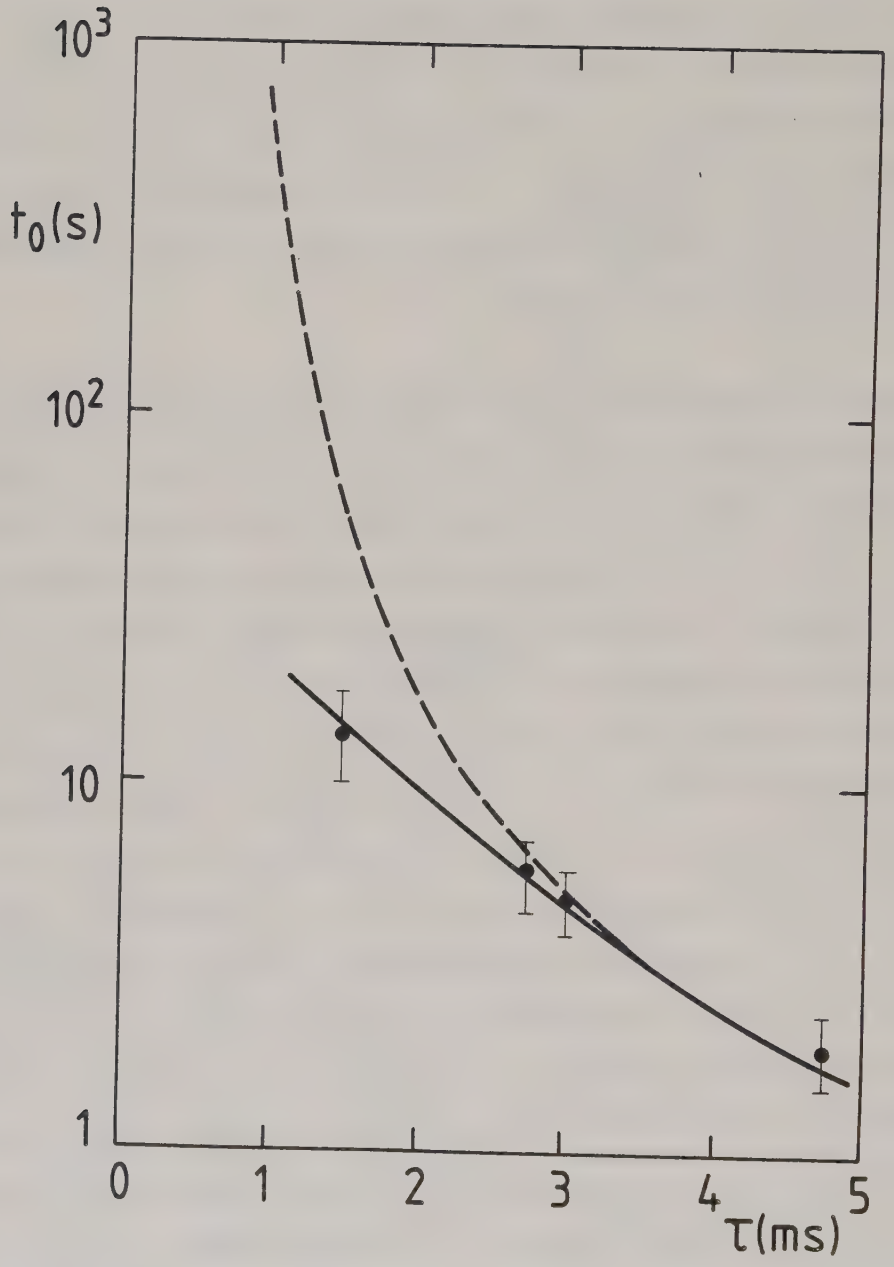


Figure E4 - Evolution du temps caractéristique t_o de décroissance des échos stimulés en fonction du temps de préparation τ dans N_2-Ar ($X_{N_2} = 0.67$) à T=4.2K. La courbe obtenue pour l'azote pur est indiquée en tireté.

des échos stimulés dans le cadre d'un modèle simplifié de diffusion spectrale dans une raie large (voir figure E5). Il est remarquable de constater qu'un modèle aussi simple fournisse une décroissance des échos stimulés qui présente une relaxation en partie logarithmique avec un temps caractéristique t_o montrant une dépendance vis-à-vis du temps de préparation proche de celle observée expérimentalement. Nous pensons que la loi logarithmique expérimentale traduit la grande diversité des contacts thermiques entre molécules voisines via les interactions dipolaires intermoléculaires, et que l'introduction de cette dispersion des couplages thermiques dans un modèle de diffusion spectrale conduirait à une relaxation logarithmique sur une large échelle de temps. Un modèle réaliste consisterait par exemple à prendre entre molécules différant de $\Delta\omega$ en fréquence et couplées par un hamiltonien flip-flop de fréquence caractéristique d un contact thermique proportionnel à $d^2 \exp-\left(\frac{\Delta\omega}{d}\right)^2$ et à supposer que les molécules sont orientées aléatoirement.

5. RESULTATS COMPLEMENTAIRES

Nous avons étudié aussi un échantillon de concentration en azote plus faible, $X_{N_2} = 0.61$, pour lequel nous avons observé exactement le même phénomène d'apparition d'un ordre de type vitreux à basse température. L'évolution avec la température du spectre RMN est montrée sur la figure E6 et est commentée dans la légende. L'apparition du verre orientationnel ne dépend donc pas de façon critique de la concentration à l'intérieur de la plage d'existence de la phase hexagonale.

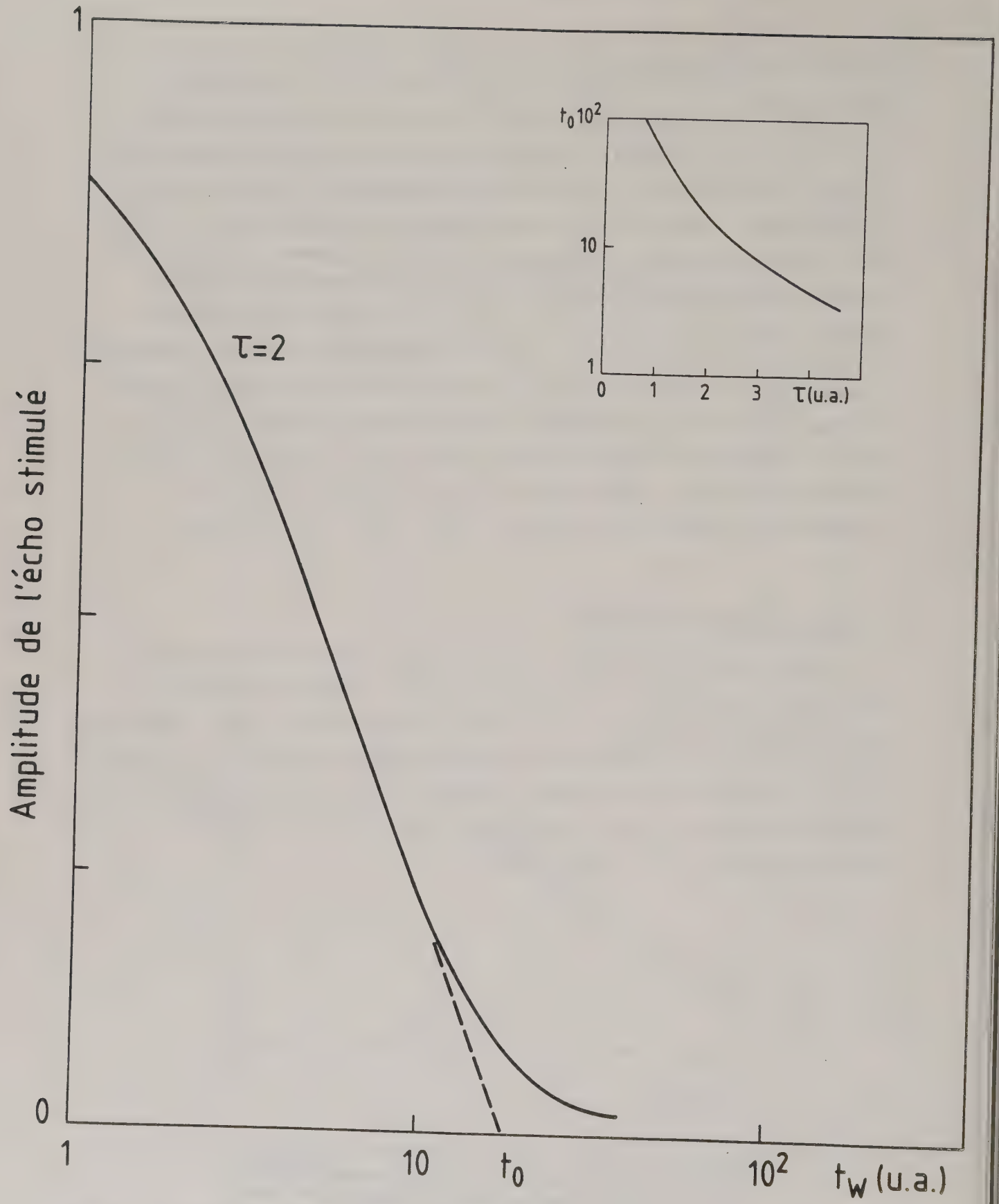
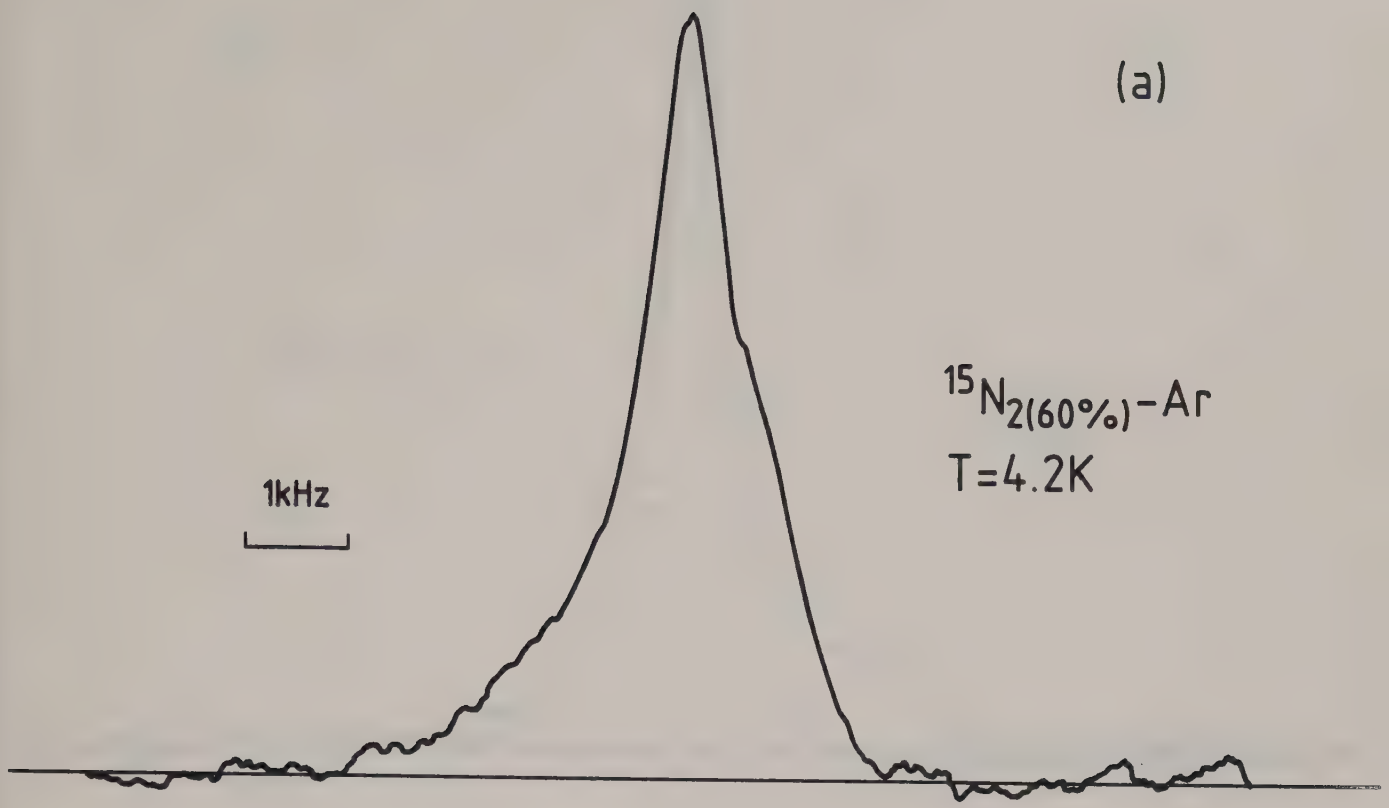
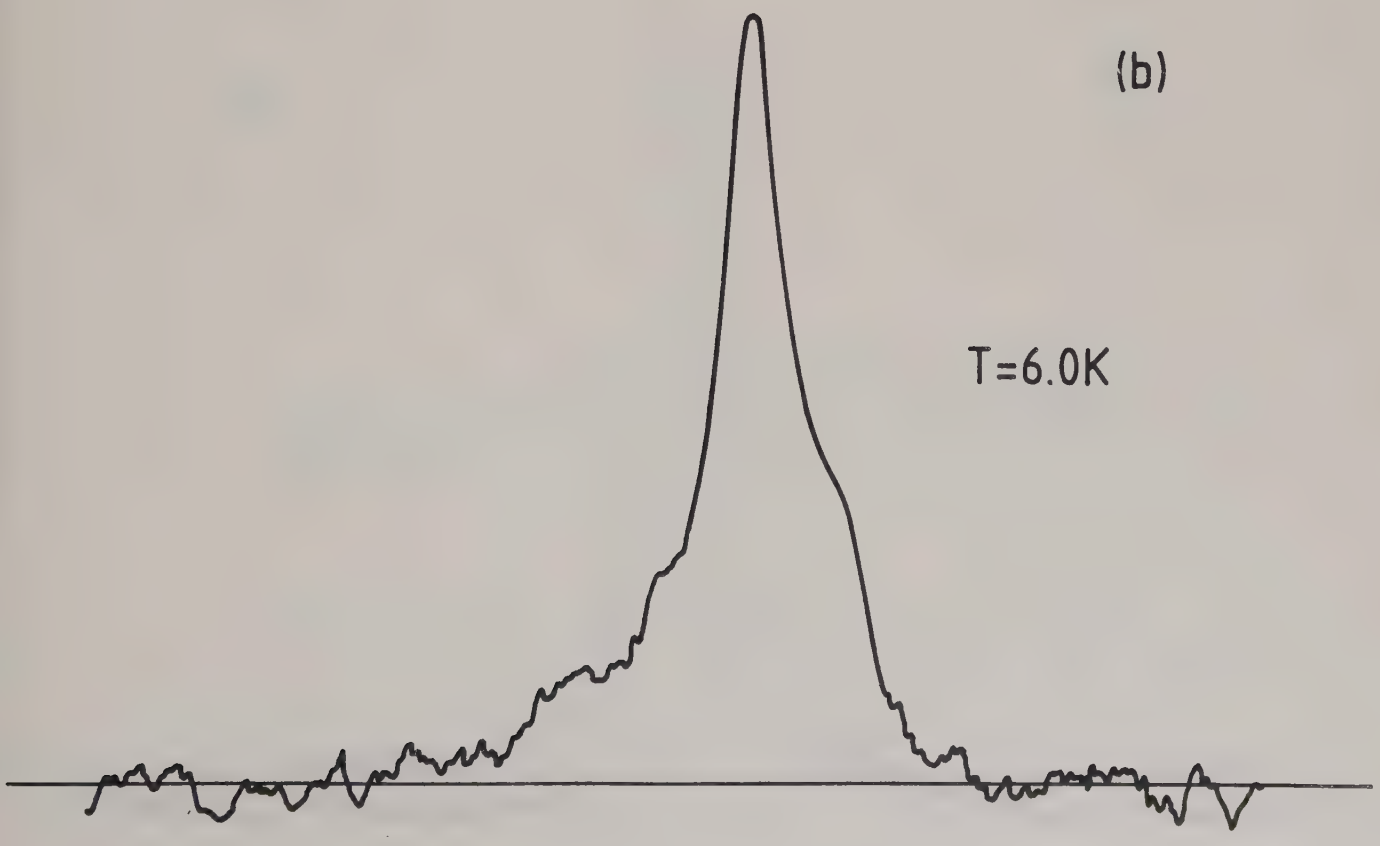
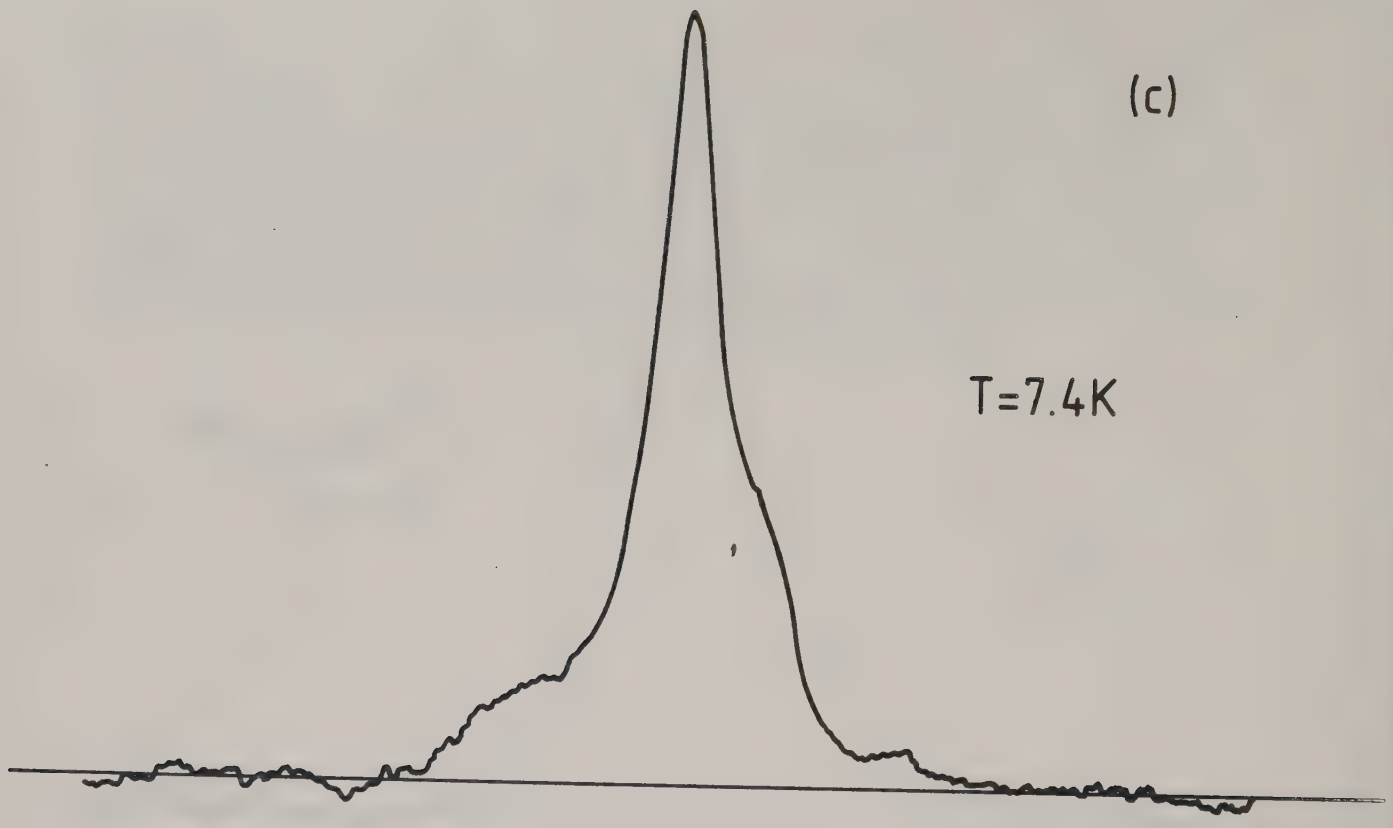


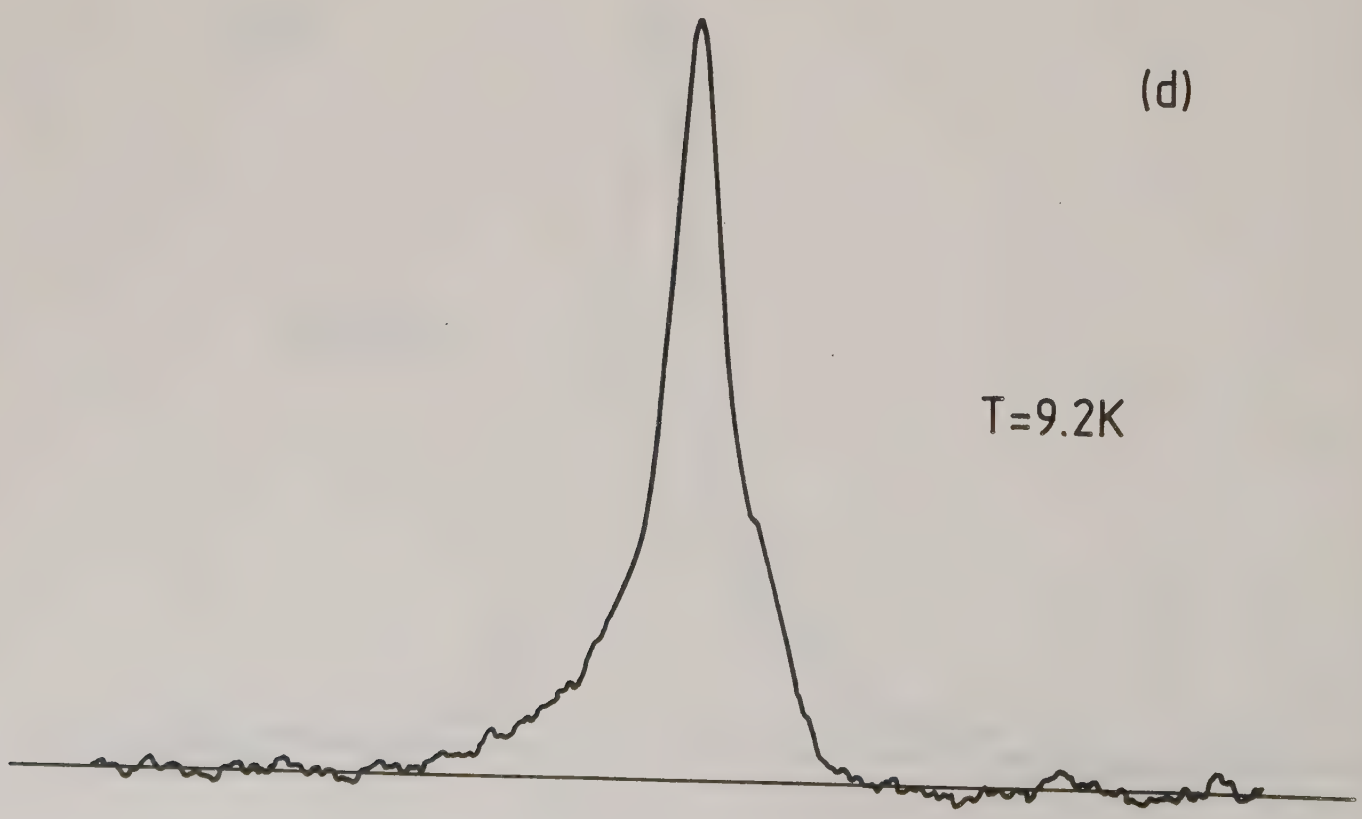
Figure E5 - Décroissance de l'écho stimulé obtenue dans le cadre du modèle simplifié de diffusion spectrale à l'intérieur d'une raie large ($-1<\omega<1, S(\omega)=1-\omega^2$) avec un contact thermique constant entre composantes de fréquences voisines. Le temps t_o qui caractérise l'amortissement est donné en encart pour plusieurs valeurs du temps de préparation τ. Les unités de temps sont arbitraires.

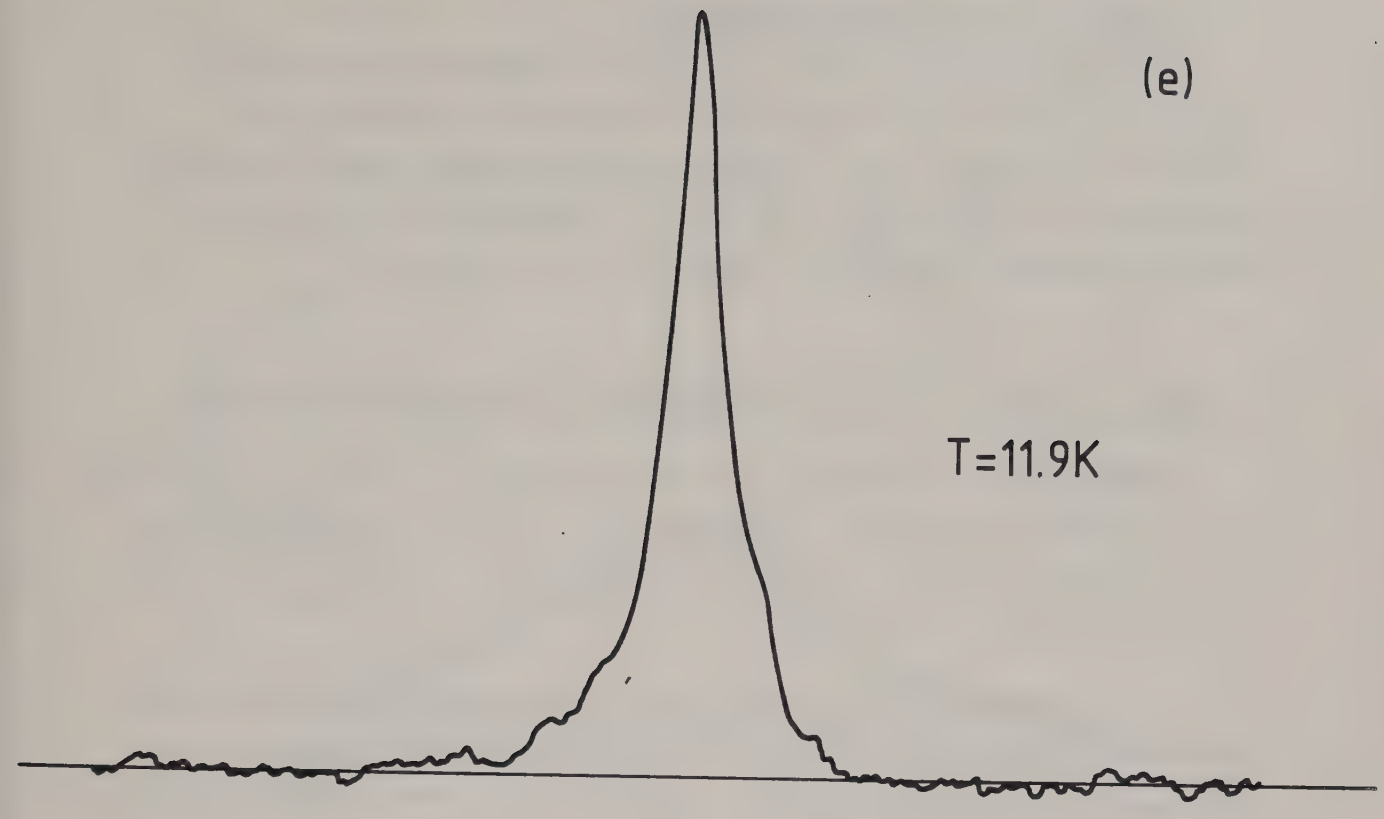
Figure E6 - Spectres RMN de ($^{15}N_{2\,0.61} - Ar_{0.39}$) à diverses températures pour $\omega_L = 2.9$ MHz. On observe à $T \lesssim 6K$ un spectre qui ne varie plus caractérisé par une distribution de quadrupolarisations pluslarge que dans l'échantillon $X_{N_2} = 0.675$ (l'épaule de droite n'est que peu visible). L'évolution du spectre aux températures supérieures s'effectue de façon progressive, l'essentiel de cette évolution s'opèrent dans la plage de température 9K-15K. Cette évolution prend donc globalement place à des températures légèrement plus basses (comparer 9K à 10K) que pour l'échantillon $X_{N_2} \simeq 0.675$ mais est qualitativement très semblable.

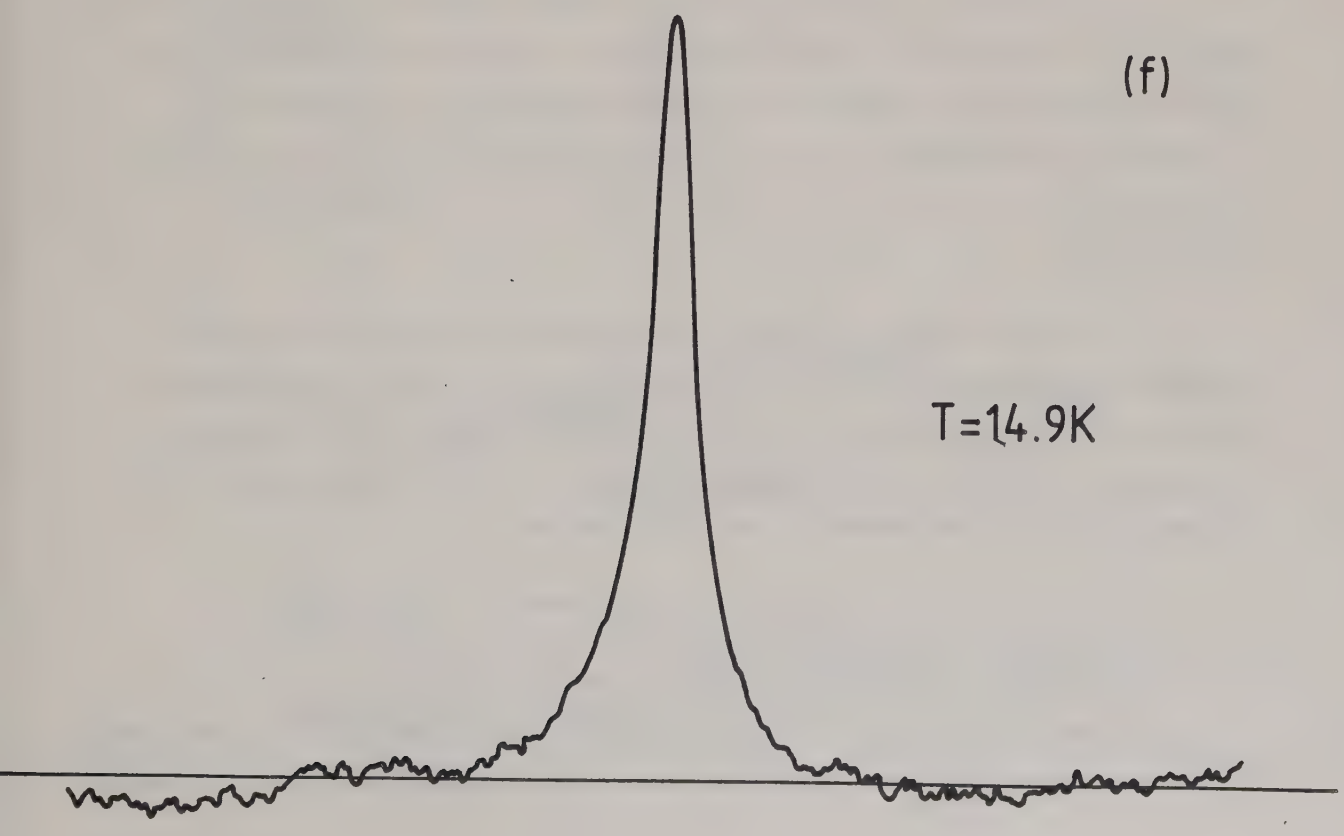

(a)
$^{15}N_{2(60\%)}$-Ar
T=4.2K
1kHz


(b)
T=6.0K


(c)
T=7.4K


(d)
T=9.2K


(e)
T=11.9K


(f)
T=14.9K

II. SYNTHESE DES RESULTATS EXPERIMENTAUX

Les mélanges N_2-Ar ont fait l'objet de travaux récents dont les résultats sont en cours de publication. Nous nous appuierons, dans cet essai de synthèse, sur l'étude par diffusion de neutrons thermiques de Press et al. [PJG82](KFA, Jülich) et les mesures de chaleur spécifique de Haase et al.[WSH83](N^{th}Carolina State University).

1. MISE EN EVIDENCE D'UN GEL ORIENTATIONNEL PAR DIFFUSION DE NEUTRONS

Press, Janik et Grimm ont effectué des mesures de diffusion élastique et inélastique de neutrons thermiques sur un mélange $N_{2(0.72)}-Ar_{(0.28)}$ pour plusieurs valeurs du moment de transfert et à diverses températures. Leurs principales observations et conclusions sont les suivantes :

a) Le système reste en phase hexagonale jusqu'à température nulle selon toute probabilité. Le spectre de diffraction d'un monocristal ne montre pas de réflexion indiquant la présence d'un ordre orientationnel à longue distance à toute température.

b) La diffusion élastique croît de façon importante lorsque la température de l'échantillon passe de $T \sim 20K$ à $T \sim 10K$ (voir figure E7). Ils l'interprètent par l'apparition progressive d'un gel orientationnel ("frozen-in orientational disorder") des molécules d'azote, sur l'échelle de temps de leur sonde, soit environ 10^{-11}s pour la résolution de leur spectromètre.

c) A basse température, les orientations des molécules d'azote présentent des corrélations à courte portée, mais pas d'ordre à longue distance. Ceci prouve que la localisation des orientations observée correspond bien à un verre orientationnel, et que ce verre résulte des interactions orientationnelles entre molécules.

2. LE LIEN AVEC LES EXPERIENCES RMN

Ces résultats obtenus avec une sonde "haute fréquence" (10^{11}Hz) sont clairement en accord avec ceux que nous avons obtenu à l'aide d'une sonde

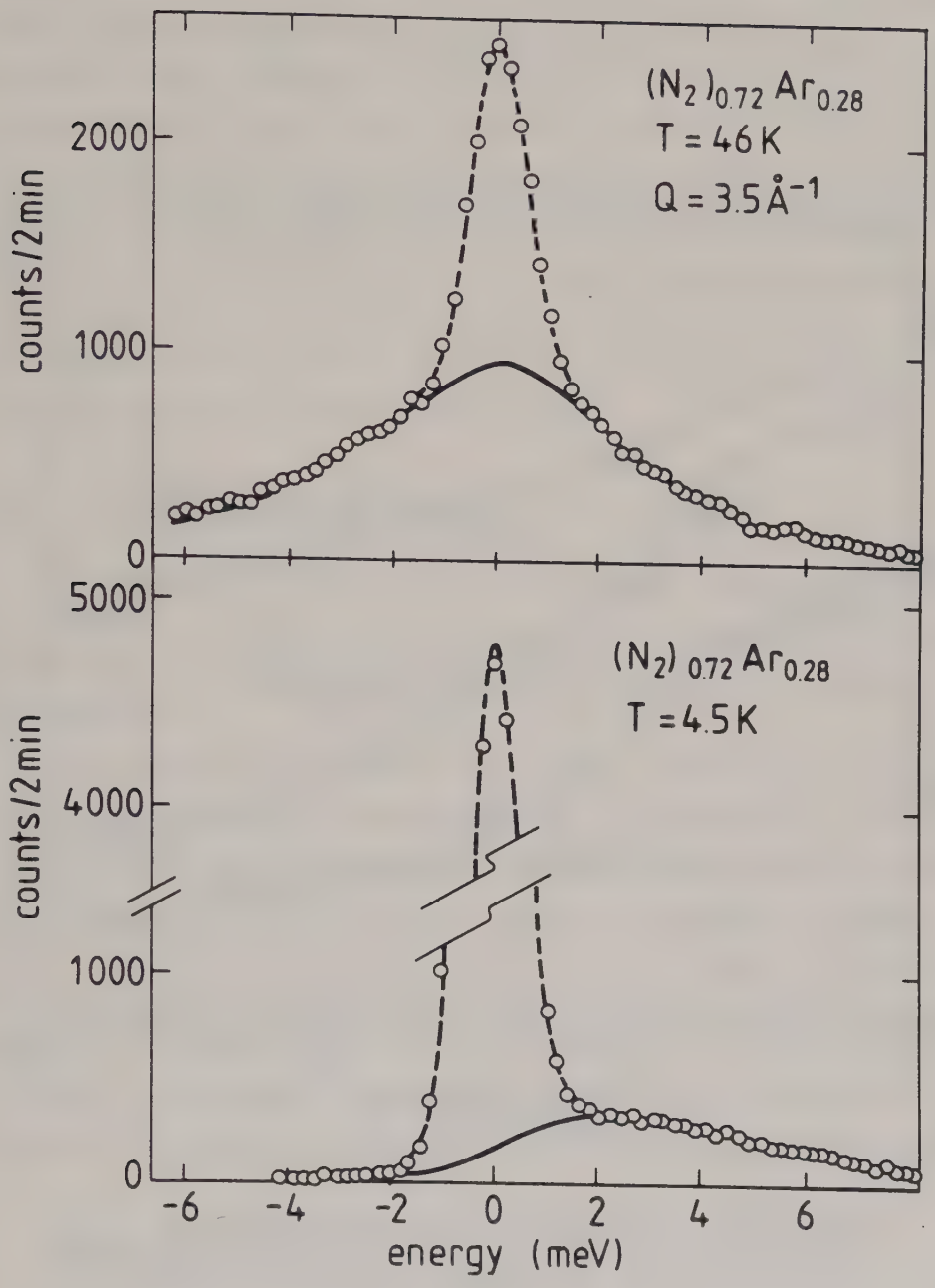


Figure E7a - Comparaison de la diffusion des neutrons dans $N2_{0.72}$ - $Ar_{0.28}$ à 46K et 4.5K. La fonction de fit du pic élastique est une gaussienne dont la largeur dépend peu de la température. D'après [PJG82].

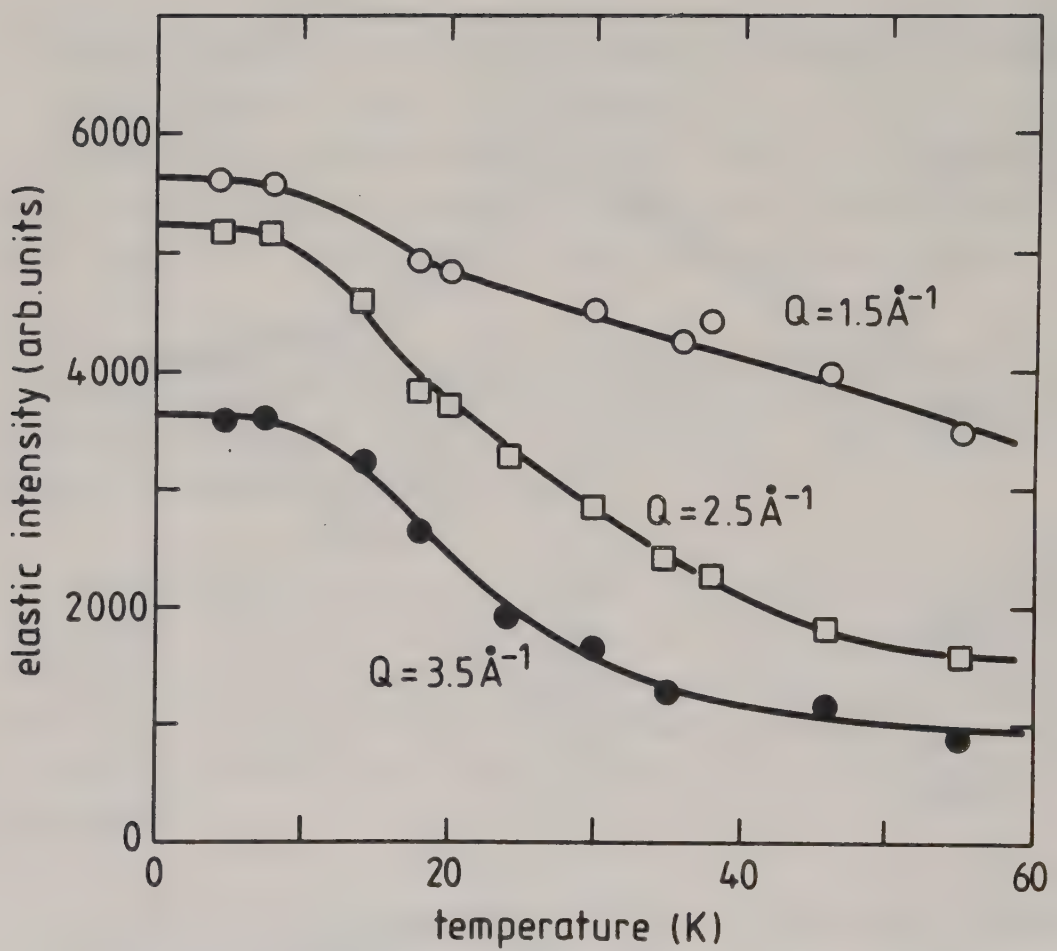


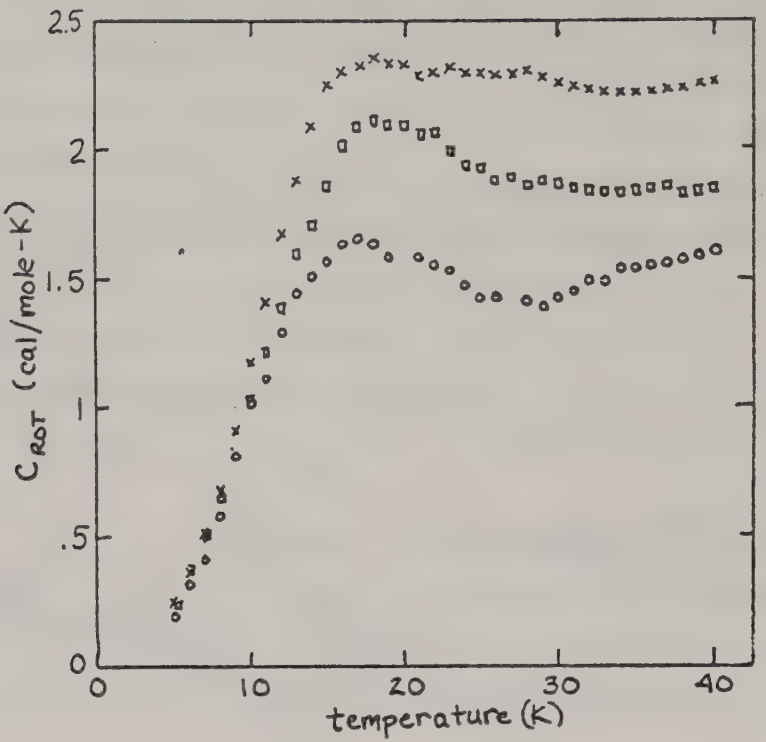
Figure E7b - Evolution avec la température de l'intensité de la diffusion élastique pour plusieurs valeurs du moment de transfert. D'après [PJG82].

"basse fréquence" (10^{-2}Hz → 10^{3}Hz) : La croissance de la diffusion élastique et la poussée des quadrupolarisations lorsque l'on refroidit l'échantillon traduisent toutes deux la localisation orientationnelle progressive des molécules d'azote. Cette identité de comportement entre deux sondes de fréquences caractéristiques si différentes semble indiquer qu'à toute température les molécules ont des "orientations moyennes" stables dans le temps et que leurs fluctuations orientationnelles autour de ces orientations moyennes restent toujours très rapides (préciser ces idées nécessiterait d'établir quantitativement le lien qui existe entre les quadrupolarisations quasi-statiques observées par RMN et l'intensité du pic de diffusion élastique des neutrons). L'image qui se dégage correspond donc à l'apparition progressive d'un verre orientationnel lorsque la température diminue.

3. LES MESURES DE CHALEUR SPECIFIQUE (Figure E8)

Les mesures de chaleur spécifique des mélanges azote-argon entreprises par Haase et al. avaient pour but essentiel de détecter une éventuelle anomalie de la chaleur spécifique rotationnelle et de possibles effets d'hysthérésis.

Les résultats sont clairs : la chaleur spécifique rotationnelle ne présente qu'une variation régulière avec la température, en accord avec la localisation progressive des orientations moléculaires que nous avons observée . Il n'y a pas de plus d'effet d'hystérésis notable observable : l'apparition du verre orientationnel s'effectue sans que des mouvements lents d'ensemble prennent place, comme le montrent par ailleurs les échos stimulés. Ce comportement est très différent de celui des verres conventionnels, pour lesquels l'apparition de la phase vitreuse autour de la température de gel s'accompagne d'importants phénomènes de relaxation lente.



E8 - Chaleur spécifique rotationnelle des mélanges (N_2-Ar)

× : $X_{N_2} = 0.70$; □ : $X_{N_2} = 0.63$; o : $X_{N_2} = 0.53$ d'après [WSH83]

4. VERS UNE SYNTHESE DES RESULTATS EXPERIMENTAUX

Nous séparerons ici le problème de la caractérisation d'un verre orientationnel à basse température de celui de sa formation.

Le premier point semble maintenant bien établi. Pour une concentration en azote de l'ordre de 0.7, les mélanges azote-argon présentent à basse température ($T \lesssim 10K$) une phase dans laquelle les molécules sont très localisées orientationnellement. Leurs orientations moyennes sont stables dans le temps, et présentent des corrélations à courte portée. Ce verre orientationnel est l'analogue pour les orientations du verre ordinaire pour les positions et du verre de spin pour les systèmes magnétiques.

Le second point est moins bien analysé. Toutes les expériences indiquent une localisation progressive des orientations moléculaires lorsque l'on abaisse la température.

Une question essentielle à laquelle n'ont cependant pas répondu les expériences est celle de l'ergodicité du système : le verre orientationnel que l'on observe est-il ou non un état d'équilibre thermodynamique ? Résulte-t-il d'un phénomène coopératif ou bien n'est il que la conséquence du désordre substitutionnel local ?

L'obtention de réponses à ces questions passe par la réalisation d'une nouvelle génération d'expériences destinées à tester la présence des phénomènes qui accompagnent les systèmes hors d'équilibre. Quelques spéculations théoriques sont présentées dans la partie F à ce propos.

III. COMPARAISON AVEC D'AUTRES SYSTEMES "VITREUX"

1. COMPARAISON AVEC L'HYDROGENE SOLIDE

Une des motivations de cette étude était d'évaluer l'importance de l'aspect quantique/classique des quadrupoles dans la formation d'un verre. Les résultats expérimentaux présentés montrent qu'un ordre de type vitreux existe aussi dans les systèmes dilués de quadrupoles classiques. Les corrélations quantiques, responsables dans l'hydrogène solide de la largeur importante de la distribution de quadrupolarisation à

basse température, apparaissent de façon beaucoup moins marquée dans les mélanges azote-argon et n'obèrent pas la formation d'un verre. L'existence de ce dernier semble plutôt résulter des effets conjugués de la frustration et du désordre, présents aussi bien dans le cas de quadrupoles quantiques que dans celui de quadrupoles classiques.

De même, la façon dont le verre apparait lorsque la température diminue ne semble pas dépendre de l'aspect quantique ou classique des quadrupoles.

Nous pensons que l'ensemble des données expérimentales recueillies tant sur l'hydrogène solide que sur les mélanges azote-argon décrivent un seul objet : le verre de quadrupoles.

2. COMPARAISON AVEC D'AUTRES SOLIDES MOLECULAIRES DILUES

L'analogie entre les systèmes magnétiques désordonnés et les solides moléculaires dilués a entraîné une recherche systématique des solides moléculaires (ou ioniques) pouvant être dilués. Dans la lignée des systèmes dilués de quadrupoles (oH_2-pH_2 , pD_2-oD_2 , N_2-Ar), il existe les systèmes dilués d'octupoles tels que CH_4-Kr ou CD_4-Kr. Ces systèmes peuvent être étudiés par diffraction de neutrons (étude non publiée de Buchenau, Maniawski et Press) et par RMN [CCLM81]. Un verre d'octupoles semble de même exister dans ces mélanges.

Un autre type de système mettant en jeu des interactions multipolaires encore plus complexes est constitué par les solides ioniques de la famille K CN-Br. Les ions CN^- présentent entre eux des interactions orientationnelles qui trouvent leur origine dans le couplage entre l'orientation de l'ion CN^- et la position des ions alcalins K^+ qui l'environnent. L'étude de ces composés*[LFK82 et références à l'intérieur] à l'aide de techniques très variées (susceptibilité diélectrique, propagation des ultrasons, diffusion de neutrons) dont les fréquences caractéristiques vont de 10^2Hz à 10^{11}Hz a montré l'existence d'un ralentissement progressif des mouvements de rotation des ions CN^- sans transition brutale lorsque la température diminue. Ce ralentissement ne peut par ailleurs s'interpréter en termes d'une loi d'Arrhenius sans invoquer des énergies d'activation irréalistes

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*Ces travaux s'inscrivent dans la lignée de ceux de Känzig sur les couplages à grande distance d'impuretés O_2^- dans une matrice de KCl[K62].

de l'ordre de 10^3K, alors que la "température de gel" est de l'ordre de quelques dizaines de K. Il s'agit donc d'un phénomène coopératif, provoqué par les interactions orientationnelles entre ions CN^-.

Le "scénario" de la formation du verre semble toutefois différent de celui qu'adoptent les systèmes dilués de quadrupoles. On constate une fois encore que si l'existence d'un ordre de type vitreux est courante dans les systèmes frustrés désordonnés, les modalités de son apparition (transition, gel dynamique, ...) sont beaucoup moins universelles.

PARTIE F :

SIMULATION NUMERIQUE D'UN SYSTEME DE QUADRUPOLES EN INTERACTION

INTRODUCTION

I - LA COOPERATIVITE DANS LA FORMATION DU VERRE ORIENTATIONNEL

II - LE SYSTEME SANS DÉSORDRE

INTRODUCTION

Nous avons montré dans la partie B qu'au point de vue orientationnel l'azote solide et les mélanges azote-argon sont essentiellement des systèmes de quadrupoles classiques en interaction. La simulation numérique est actuellement la méthode la plus puissante dont on dispose pour appréhender le problème de l'ordre orientationnel dans de tels systèmes. Nous l'avons utilisée principalement pour évaluer le degré de la coopérativité impliquée dans la formation du verre orientationnel (§.I). Nous avons aussi étudié le problème de l'ordre orientationnel en l'absence de désordre (§.II) pour le réseau cfc (à titre de vérification) et pour le réseau hc qui semble présenter une pathologie particulière.

I - LA COOPERATIVITE DANS LA FORMATION DU VERRE ORIENTATIONNEL

1) ARTICLE :

" EVIDENCE FOR COOPERATIVITY IN QUADRUPOLAR GLASS FREEZING FROM MONTE CARLO SIMULATIONS "

EVIDENCE FOR COOPERATIVITY IN QUADRUPOLAR GLASS FREEZING FROM MONTE CARLO SIMULATIONS

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ABSTRACT

We present a Monte Carlo study of a dilute system of interacting classical quadrupoles on an hcp lattice for quadrupole concentrations X = 0.68 and X = 0.53. Within our computation time limits which were 4 10^5 MCS per quadrupole for a sample of 96 sites and 10^5 MCS per quadrupole for a sample of 216 sites, we find a progressive growth of the local quadrupolarisations. However, an analysis of the orientational fluctuations sets a lower bound of the order of 100 on the number of correlated quadrupoles responsible for this growth.

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I. INTRODUCTION

It is now generally accepted that at low temperatures dilute systems of quadrupoles such as ortho-para mixtures of hydrogen or deuterium present a glassy state in which the quadrupole bearing molecules (angular momentum J=1) adopt essentially random orientations from one crystal site to another (Silvera 1980). This view has received recent confirmation from NMR measurements in N_2-Ar mixtures which present the same overall low temperature features as the solid hydrogen mixtures (Esteve et al 1982a) ; the differences lie in the properties of the N_2 molecule which behaves as a classical rotator when compared with the H_2 molecule which behaves as a quantum one.

However, the manner by which the glass state is established on cooling is still subject to an intense debate.

Two kinds of behaviour have been postulated. In the first one, a parallel is drawn (Sullivan et al 1978) between the dilute systems of quadrupoles (DSQ) and spin glasses such as $Cu_{1-x}Mn_x$ or $Eu_x Sr_{1-x}S$. This parallel finds its justification in the combination of frustration and disorder that occurs in both spin glasses and DSQ. Following this analogy, the quadrupoles would freeze in their random ground state configuration by a cooperative process * similar to that which occurs in spin glasses (although the spin glass transition is still not completely understood there is however no question that it is a cooperative phenomenon involving a large number of spins (Toulouse 1982).

In the second point of view, one insists on the peculiarity

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* An ansatz for the evaluation of cooperativity -i.e. of the number of particle involved in a cooperative behaviour- of an N particle system is the evaluation of the minimal size of a finite system which reproduces the properties of a portion of the same size in the infinite system. For example in the Ising model, this size goes from 1 at infinite temperature to infinity at the transition temperature.

DSQ's to have their local symmetry always broken even at high tempe-peratures (Esteve et al 1982b, Washburn et al 1982). This effect can be briefly described as follows : when two axial quadrupoles rotate randomly while maintaining interaction-mediated correlations each one produces on the other a fluctuating field gradient which does not average to zero ; on the contrary, for a pair of dipoles, the fluctuating fields always average to zero regardless of their strength and the nature of the coupling provided it is bilinear. The difference between dipoles and axial quadrupoles is that a configuration of dipoles has always a mirror configuration of the same energy obtained by inverting all dipoles while axial quadrupoles lack such a fundamental symmetry property. Thus, a quadrupole whose neighbours do not form a symmetric shell (and this happens when the concentration of quadrupoles departs either from 1 or 0) will experience a static field gradient that will essentially be "directed" along the portion of the shell where the greater number of quadrupoles are present. At temperatures T much greater than the typical energy scale Γ of the quadrupolar interaction, only pair correlations will be important. The orientation of the field gradient will then be constant and entirely determined by the local surroundings of a molecule while its magnitude will vary as Γ/T. Consequently, one could think that this effect would remain dominant at low temperatures $T \lesssim \Gamma$ (although correlations could become more complex, they would involve essentially only a few quadrupoles) and that the system would be driven smoothly towards its ground state as the temperature is reduced, any strong cooperativity being suppressed by the broken symmetry. The ordering would essentially be determined by the local disposition of occupied lattice sites. This view is supported experimentally by the absence of any singularity or hysteresis in a certain class of experiments made by some authors (Washburn et al 1982, Candela et al 1980). They have even been led to question the application of the term "glass" to the low temperature state of the system (Washburn et al 1982).

The aim of the Monte Carlo simulations reported in this paper is to decide whether the observed tendency of the quadrupoles to align at low temperature along certain directions is due to a weakly cooperative effect (involving only very local correlations) or a

strongly cooperative effect (involving a great number, perhaps infinite, of correlated quadrupoles). Previous numerical experiments were concerned with the T=0 properties of the DSQ and did not address the question of their evolution with temperature (Klenin and Pate 1981).

II. COMPUTATIONAL PROCEDURES

1) The quadrupolar Hamiltonian

The solid hydrogens or N_2-Ar mixtures can be very satisfactorily described, as far as orientational degrees of freedom are concerned, by an effective quadrupole-quadrupole Hamiltonian (Silvera 1980, Scott 1976) which can be written as :

$$\mathcal{H} = \sum_{<ij>} \Gamma_{ijmn} \, \mathcal{Q}_{im} \, \mathcal{Q}_{jn}$$

where <ij> denotes a pair of occupied sites and $\mathcal{Q}_{im}$ the real irreducible tensorial components of the quadrupole at site i (the $\mathcal{Q}_{im}$ are the equivalent of the components S_x, S_y, S_z for a dipole).

$$\begin{aligned}
\mathcal{Q}_0 &= \gamma^2 - \frac{\alpha^2+\beta^2}{2} \\
\mathcal{Q}_1 &= \sqrt{3}\,\beta\gamma \\
\mathcal{Q}_2 &= \sqrt{3}\,\gamma\alpha \\
\mathcal{Q}_3 &= \sqrt{3}\,\alpha\beta \\
\mathcal{Q}_4 &= \frac{\sqrt{3}}{2}(\alpha^2-\beta^2)
\end{aligned}$$

where α, β, γ are the direction cosines of the quadrupole. The $\mathcal{Q}$'s are operators in the manifold J=1 for the hydrogens and ordinary c-numbers in the case of N_2-Ar mixtures.

Γ_{ijmn} is the interaction matrix which is written as

$$\Gamma_{ijmn} = \frac{4}{3}\,\Gamma\, a_m\, \delta_{mn}$$

for a particular choice of the reference frame in which the $\hat{z}$ axis

coïncides with the vector $\vec{R}$ joining the centre of the two quadrupoles while a_m is given by :

$$a_m = [6, -4, -4, 1, 1]$$

Γ is the energy scale which is chosen so that the lowest energy of the pair is -4Γ. For classical quadrupoles :

$$\Gamma = \frac{3}{4} \frac{Q^2}{R^5}$$

where Q is the effective quadrupole moment of the molecule*. In general Γ_{ij}^{mm} depends on the direction cosines of $\vec{R}$ relative to the reference frame.

2. The simulation algorithm

We have performed a Monte Carlo simulation using Hamiltonian (1) for a system of classical quadrupoles randomly distributed on an hcp lattice which is believed to describe the crystal structure of solid hydrogens and N_2-Ar mixtures in the glass regime (Silvera 1980). The interaction was limited to first neighbours as this is considered to be a good approximation in the pure case (Mandell 1974, Sullivan 1976). The number of sites of the lattice was 96 in most of the runs but was extended to 216 on some runs to investigate size effects. Periodic boundary conditions were used. In the 96 site lattice, the number of quadrupoles was N=65 (i.e. a concentration X=0.68**) in one sample and N=51 (X=0.53) in the other. In the 216 site lattice, this number was N=151 (X=0.70).

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* For quantum quadrupoles (J=1) $\Gamma = \frac{6}{25} \frac{Q^2}{R^5}$. The majority of papers retain this latter definition for classical quadrupoles but in this case the lowest pair energy is $-25/2\ \Gamma$.

** The availability of experimental data on N_2-Ar mixtures (Esteve et al 1982a) at this concentration motivated this choice.

The Monte Carlo algorithm we used was a simple generalization of the standard rejection algorithm for Ising spins (Hammersley and Handscomb 1964), the number n of spin states being extended from 2 to 48. These 48 states corresponded to 48 quadrupolar orientations distributed as uniformly as possible on the half sphere and verifying

$$\sum_n Q_m(\alpha_n, \beta_n, \gamma_n) = 0$$

in order to avoid a trivial one-particle anisotropy.

The discretness of quadrupolar orientations is of no consequence as soon as $T >> \frac{\Gamma}{N}$. This was checked by varying n from 27 to 48.

The motivation for this discretization of quadrupolar orientations was that a table of energies could be constructed and the necessity of computing the rather complex interaction energy at each Monte Carlo step (MCS) was avoided, thus allowing us to attain 3.10^5 MCS per quadrupole at a given temperature. No attempt was made to use a more sophisticated Monte Carlo algorithm (Borz et al 1975) since we did not go to very low temperatures where the rate of successful flips become disastrously small.

Our algorithm was tested on a non-dilute system of 108 interacting quadrupoles on the fcc lattice. On lowering the temperature the system could nucleate and develop the well known long range ordered pa3 structure (Silvera 1980) at the correct transition temperature (Mandell 1974) ($T_c \approx 3.5\Gamma$ with our definition of Γ) in less than $3\ 10^6$ MCS.

Our computational ressources were distributed between two kinds of experiments

i) Standard coolings of the system by varying the temperature step by step, each step yielding a run of 10^6 to $5\ 10^6$ MCS. The average cooling rate was fixed by the magnitude of the temperature steps (10^7 MCS per unit of the reduced temperature -u.r.t.- T/Γ).

ii) Very long cooling runs ($3\ 10^8$ MCS) with extremely slow cooling rates at low temperature (up to $5\ 10^8$ MCS/u.r.t.).

3. Analysis of the Monte Carlo runs

For each temperature step, the program calculated the average energy and constructed a histogram of the successive orientations adopted by each molecule during the time slice of the step. At the end of the cooling run, the histograms were used to produce for each time slice a table of the average quadrupolar moments Q_{im} of each molecule :

$$Q_{im} = [\mathcal{Q}_{im}]_{\Delta t}$$

These moments can be regrouped into a temporal average of the local quadrupolar tensor symbolized by $\bar{\bar{Q}}_i$. This table of average quadrupolar tensors reflects the average orientational state of the system of quadrupoles during a time slice Δt.

Following the extraction of the local average quadrupolar tensors from the histograms, a suitable rotation of local frames were performed in order to diagonalize the average cartesian quadrupolar tensor $q_{\alpha\beta}$

$$q_{\alpha\beta} = \begin{bmatrix} -\frac{Q_0}{3} + \frac{1}{\sqrt{3}} Q_4 & \frac{1}{\sqrt{3}} Q_3 & \frac{1}{\sqrt{3}} Q_2 \\ \frac{1}{\sqrt{3}} Q_3 & -\frac{Q_0}{3} - \frac{1}{\sqrt{3}} Q_4 & \frac{1}{\sqrt{3}} Q_1 \\ \frac{1}{\sqrt{3}} Q_2 & \frac{1}{\sqrt{3}} Q_1 & \frac{2}{3} Q_0 \end{bmatrix}$$

This operation transforms the irreducible components Q_{im} into new ones Q'_{im} which are of the form :

$$Q'_{i0} = \sigma_i$$
$$Q'_{i1} = Q'_{i2} = Q'_{i3} = 0$$
$$Q'_{i4} = \eta$$

There is no ambiguity in the choice of the new local frame if one imposes $\eta \geq 0$ and $|\sigma| > \sqrt{3}\eta$. Since the distribution function of

the invariants σ and η is related to the NMR lineshape (Esteve et al 1982a) in the solid ortho-para H_2, D_2 and N_2-Ar mixtures, this distribution was constructed for each run.

A convenient quantity which measures to which extent the quadrupoles are oriented regardless of the particular "shape" of the quadrupolar tensor is the quadratic average q over all occupied sites of the average local quadrupolarisation x_i over a duration Δt.

$$q = \subset x_i^2 \supset \quad \text{with} \quad x_i = (\sigma_i^2 + \eta_i^2)^{\frac{1}{2}}$$

$\subset \ldots \supset$ denotes an average on all quadrupoles. q is the analogous of the quadratic average of the local polarisation of a dipolar system i.e. the Edwards and Anderson order parameter (Edwards and Anderson 1975).

In order to compare the different average states produced by different time slices within one run or between different runs, we have used two kinds of projections. These projections are based on the scalar product of two average quadrupolar tensors :

$$\bar{\bar{Q}} \cdot \bar{\bar{Q}}' = \sum_m Q_m Q'_m$$

and their "cosine" :

$$\cos(\bar{\bar{Q}}, \bar{\bar{Q}}') = \frac{\bar{\bar{Q}} \cdot \bar{\bar{Q}}'}{(\bar{\bar{Q}} \cdot \bar{\bar{Q}})^{\frac{1}{2}} (\bar{\bar{Q}}' \cdot \bar{\bar{Q}}')^{\frac{1}{2}}}$$

This generalized cosine function depends on the respective orientations of the principal axes and on the relative aspect ratio σ/η of the two quadrupolar tensors.

The first projection is an ordinary projection along the "direc-

tion" of a reference average orientational state :

$$\Pi_1 = \subset \frac{\bar{\bar{Q}}_i \cdot \bar{\bar{Q}}_i^0}{(\bar{\bar{Q}}_i^0 \cdot \bar{\bar{Q}}_i^0)^{\frac{1}{2}}} \supset$$

The second projection is an average over all cosines :

$$\Pi_2 = \subset \cos(\bar{\bar{Q}}_i, \bar{\bar{Q}}_i^0) \supset$$

III. RESULTS AND DISCUSSION

1. General results

We have obtained the energy of the system as a function of temperature. The results are plotted in Figure (1) and were very reproducible from one run to another above $T/\Gamma \sim 1$. Below $T/\Gamma \sim 1$ the scatter rose to 3%. We interpret this scatter as the consequence of the inability of the system to sample configuration space correctly in the time allowed for the calculation. As will be shown later, thermodynamical equilibrium was not reached in this temperature range. The points below $T/\Gamma \sim 1$ given in Figure (1) should thus only considered as upper bounds of the true energy. Furthermore, the discretness of orientations may have prevented the system from reaching its lowest energy state.

However, one notices that the energy curve is smooth, in contrast with the pure system of quadrupoles on the fcc lattice (Mandell 1974).

This smooth behavior is also found in the evolution of the local quadrupolarisations : These quadrupolarisation have a broad distribution (see Figure 2) especially in the intermediate temperature range $T/\Gamma \simeq 2 \rightarrow 1$ (for the X = 0.68 sample) where most of the evolution takes place. Below $T/\Gamma \simeq 1$, they reach values close to one : the quadrupoles are then almost completely frozen, without any long range order, just as magnetic spins in spin glasses are frozen at low temperature.

Here again the question arises whether this glass behaviour observed for a finite number of MCS (5 10^6 MCS per temperature step) do represent thermal equilibrium properties.

In order to tackle this problem we have first examined in detail the behaviour of the system at high temperatures where it is close to the completely disordered state.

2. High temperature behaviour of the system

Calculations by Harris (1970) for mixtures of ortho and para hydrogen show that the quadratic average q of the local quadrupolarisations has a high temperature behaviour given by

$$q = \alpha \times (1-X) \left(\Gamma/T\right)^4 \qquad (2)$$

X is the concentration of quadrupoles and $\alpha = 12(25/18)^2$.

This result also holds for classical quadrupoles provided that the value of α is changed to $\alpha = 12(32/63)^2$.

In dilute systems of axial quadrupoles, q is always non-zero, in contrast to spin glasses for wich the E.A. order parameter

$$q = \overline{\langle S_i \rangle_T^2}$$

is zero above the transition temperature and in zero external field. As explained above, this property results from a combination of the symmetry properties of the quadrupolar interaction and of thermal equilibrium pair correlations. This effect makes D.S.Q. somewhat similar to spin glasses in an external field.

We have evaluated to what extent the local quadrupolarisation were a mere consequence of the local disorder in two ways by extracting from the Monte Carlo runs :

i) the values of q as a function of the temperature

ii) the π_2 projection with the high temperature state.

The results obtained for the N=65 (X=0.68) sample for time slices

of different lengths are shown in Figure 3. The values of the standard deviation $q^{1/2}$ of the local quadrupolarisations and of π_2 are compared with the predictions of the high temperature expansion up to second order in T^{-1}.

The values of π_2 obtained with 10^6 MCS show important fluctuations resulting from the difficulty of reaching thermodynamical sampling with this number of MCS. The points corresponding to 2 10^7 MCS are believed to describe an essentially correct thermodynamical average.

It can be seen that formula (2) correctly describes the results above $T/\Gamma \approx 3$ when provision is made for the background due to the finiteness of the sampling. For lower temperatures, the observed quadrupolarisations are smaller than expected. This can be produced by two effects :

i) formula (2) is only an expansion in Γ/T and overestimates $q^{1/2}$ even for a simple pair of quadrupoles for which the T=0 value of $q^{1/2}$ can be exactly calculated to be equal to $\frac{1}{4}$.

ii) the geometry of the h.c.p. lattice (or any 3D lattice) is such that the pair correlations are incompatible with one another - an effect which is the manifestation of frustration.

However the scalar product π_2 falls to zero rapidly when $T/\Gamma \lesssim 1.5$ (see Figure 3b). This shows that the orientations of local quadrupolarisations, at low temperature, are essentially quite uncorrelated with their high temperature counterparts and that effect ii) becomes dominant.

We conclude from these results that more complex correlations than pair correlations become dominant below $T/\Gamma \simeq 1.5$. A similar behaviour has been also observed for the N=51 (X=0.53) sample.

3. Analysis of the long-lived low temperature fluctuations

We now address the question of the number of particles involved in these low temperature correlations.

A clue to the number of particles lies in the behaviour of the system below $T/\Gamma \sim 1.5$ for the N=65 sample.

This behaviour is characterized by two main features (see Figure 3) :

- large fluctuations of the orientational states from one temperature to another
- an irreproducibility of the orientational state for different cooling histories of the same sample.

These features signaled the difficulty encountered by the algorithm of maintaining thermal equilibrium during a cooling history. More precisely, for a cooling rate of 10^7 MCS/u.r.t. the states obtained for different thermal histories started to deviate from one another at $T/\Gamma \sim 1.5$: the characteristic times for the evolution of configuration had become too long with respect to the number of MCS that was allocated to the experiment. We checked that these long times did not originate from a large decrease in the rate of successful MCS. They could therefore only be explained by invoking correlated motions of the quadrupoles, associated with a special type of motion of the representative point of the system in configuration space.

In order to obtain an overall view of the landscape in configuration space, we tried to classify the configurations adopted by the system at the end of the cooling histories. We analyzed the results of about 20 thermal cycles (10^7 MCS/u.r.t.). In spite of the irreproducibility of these histories, the scatter in the average orientational states that were found at $T/\Gamma \sim 1$ was only partial since by projecting every state on every other one we could identify 5 classes of states. Their energies were found to be equal at least to within thermal fluctuations. Within a class the projection π_1 between two states gave a value close to unity, thus indicating close proximity in the space of orientational states. On the contrary, the projection π_1 between two states belonging to different classes gave a small value showing that the different classes are well separated in the space of orientational states.

The different classes can be interpreted as attractive wells for the system at low temperature. The small number of classes by itself indicates that the low temperature states result from a collective compromise involving the whole sample or at least large part of it. (If a number C of small clusters having on the average S states had been involved, the number of ground states would have been of the order of S^C).

It was tempting to relate these low temperature attractive wells to the long times appearing at $T/\Gamma \lesssim 1.5$ which would correspond to the passage from one well to another above barriers in configuration space.

In order to characterize the motion of the system in configuration space, we tracked the path followed by the system by projecting the successive orientational states obtained during the very long cooling runs on different low temperature orientational states.

The results shown in Figure 4 demonstrate that in the temperature range where fluctuations are important the evolution of the system consists of sudden jumps between well defined orientational states closely corresponding to the low temperature states. Each jump correspond to a global rearrangement of all quadrupoles, that is a jump between two limited region of configuration space separated by a distance of the order of the radius of this space (distances in configuration space can be precisely defined from the scalar product given above).

The scale of cooperativity at these temperature is therefore equal to or greater than the sample size.

As the temperature is lowered the time between jumps becomes longer and longer. It takes a larger and larger number of MCS to obtain the correct orientational state. For example, the values of $q^{1/2}$ obtained with 5.10^6 MCS shown in Figure 3 are greater than the equilibrium ones below $T/\Gamma \simeq 1.5$ as indicated by averages performed over longer time slices. We estimate that at $T/\Gamma = 1.2$ it would take 10^8 MCS to obtain the correct thermodynamic value for $q^{1/2}$.

The occurence of different orientational states at low temperature can thus be interpreted as follows : during cooling, the time between jumps increases until a temperature is reached for which the jumps become longer than the subsequent observation time at lower temperatures. The system becomes thus trapped in a particular well in configuration space.

We were not able by cooling the system at a sufficiently slow rate to show that one of the wells was the dominant well which would contain the true ground state.

These cooperative jumps of the system were also observed in the N=51 sample on 96 sites but the trapping of the system took place at somewhat lower temperature ($T/\Gamma \sim 1.0$). The same jumps also occur in the 216 site sample with N=151 quadrupoles (X=0.70) although the much longer time necessary to the observation of a jump prevented us to make a thorough exploration of attractive wells.

Finally, an investigation of a sample of 17 quadrupoles on the 96 sites lattice showed no strong cooperative behaviour as expected for a sample containing only small clusters.

IV. CONCLUSION

In summary, these numerical simulations on finite samples of DSQ indicate a growth on cooling of orientational correlations until the whole sample behaves as a single entity. On further cooling, our observation time became shorter than the "ergodicity" time of the system (i.e. the minimum time for which the time average is a satisfactory makeshift of thermodynamical average).

If one now turns back to the debate presented in the introduction, i.e. is this system smoothly driven on cooling towards a unique ground-state or at the opposite extreme does it present a strongly cooperative phenomenon, one can say that the second hypothesis is supported by these results on finite samples. However, one can then ask the following question : given more computing power -which would be used to increase sample size and correspondingly the number of MCS per quadrupole- would the cooperativity reported here scale up with sample size ?

Would this regime of hopping between a few pockets in configuration space be preserved ?

In other words is the scale of cooperativity infinite ?

One can think of two different ways in which the regime of hopping would be suppressed, in going to larger and larger systems :

i) There could be a fundamental limit of the number of quadrupoles participating in a jump of the system in configuration space. The system would in that case be analogous to a super-paramagnet.

ii) The different pockets could merge and would form only one dominant well. The jumps in configuration space would then be of limited range. One cooling, the system would be driven smoothly toward one ground

state as in the case of a ferromagnet in an external field.

The different situations are schematically presented in Figure 5. In spite of the difficulty of extrapolating the results of the present work to the real infinite system, it is worth noting that they reproduce the behaviour of (N_2-Ar) solid mixtures (X_{N_2}=0.67) which in the temperature range $2 > T/\Gamma > 1$ present

1) A continuous growth of the local quadrupolarisations on cooling

2) Large distributions of quadrupolarisations

3) The absence of any singularity in the specific heat but the presence of a significant orientational contribution (Pace et al 1969)

Although the comparison between a classical system and a quantum one might be subject to caution, there is a qualitative agreement between the above features which were also observed in our X=0.53 sample and the experimental observations in solid H_2 with the same ortho concentration (Estève et al 1982b, Washburn et al 1980, Washburn et al 1982, Haase and Saleh 1981).

Let us note also that the observation in solid o-H_2/p-H_2 mixtures of a substantial slowing down of orientational fluctuations accompanied by hysteretic effects (Sullivan and Esteve 1981) has led us (Sullivan et al 1982) to hypothesize that the quadrupolar glass state was a consequence of a non-ergodic behaviour of the system. This view receives support from the present M.C. calculation.

A good agreement between Monte Carlo simulations and experimental results while the former are proven to be obtained out of equilibrium is a prevalent situation in the field of spin-glasses (Toulouse 1981) : algorithms proven to converge do not find a spin glass transition while ordinary ones (and the majority of experimentalists) do. It may well be that dilute systems of quadrupoles and spin glasses share the same numerical problems.

ACKNOWLEDGMENTS

We are indebted to N.S. Sullivan for numerous discussions and to L. de Seze and N. Tichit for their help with the use of the Prime computer. We wish to thank M. Bonnet and P. Imbert for their lending of terminal facilities. A stimulating conversation with Professor A.B. Harris is also gratefully acknowledged.

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FIGURE CAPTIONS

Figure 1 : Average energy per quadrupole of the dilute system on the hcp lattice (N=51 and N=65 samples) during a cooling run. Each dot represents 10^6 MCS. The solid lines are smooth interpolations between points. The points below $T/\Gamma \simeq 1$ are believed to be only upper bounds of the true energies in view of the difficulty of reaching the lowest energy states of the system. The error bars represent the scatter of the results between cooling runs.

Figure 2 : Evolution of the distribution of local quadrupolarisations in function of the temperature for the X=0.68 sample. Each dot correspond to the quadrupolarisation of one molecule represented in the (σ,η) plane. The solid line is the boundary of the locus of allowed (σ,η) (see text).

Figure 3 : Comparison between the average orientational states obtained from different time slices (circles : 10^6 MCS, dots and triangles : $5\ 10^6$ MCS, squares : $2\ 10^7$ MCS) and those predicted by the high temperature expansion up to second order in T^{-1} (dashed lines).

3a) full symbols : standard deviation $q^{1/2}$ of the local quadrupolarisations. The triangles and the dots correspond to different cooling runs.

3b) open symbols : projection π_2 of the average orientational state on the average orientational state obtained at $T/\Gamma = 5$ and with $2\ 10^7$ MCS.

The solid lines are only guides for the eye.

Figure 4 : Time evolution of the projection π_1 (see text) of the orientational state of the N=65 sample on different reference states during one long cooling run. Each bar represents an average taken over 10^6 MCS. In track c) the reference was the last orientational state of the run (arrow). In tracks a) and b) the references were two other orientational states obtained at the end of other cooling runs. The temperature profile of the cooling run is shown at the bottom of figure c). One observes that the sudden rises of π_1 occur alternately on the different tracks. This behaviour is interpreted as sudden jumps of the entire system between a small number of different wells in configuration space.

Figure 5 : Schematic representation of the possible topologies of energy profile in configuration space in the large N limit, N being the number of quadrupoles in the sample. The horizontal coordinate is a generalized coordinate whose purpose here is only to symbolize the configuration space continuum. The vertical coordinate is the energy per particle.

a) Small number of attractive wells separated by energy barriers. On cooling, the system is trapped in one of the wells, as symbolized by the horizontal lines which represent the volume of configuration space occupied by the system. When the energy of the system is equal to the barrier top, one observes hopping of the system between different wells, the time between jumps going to infinity in the $N \to \infty$ limit.

b) Only one well remains in the $N \to \infty$ limit. The system approaches its unique ground state continuously as the temperature is reduced, and is thus analogous to a super-paramagnet in an external field.

c) The absolute value of barrier heights remains finite in the $N \to \infty$ limit, leaving a continuum of ground state. The system is analogous to a super-paramagnet in zero field even at T=0, although its dynamics might be extremely slow.

There are intermediate situations characterized by the dependence upon N of the number of wells and the height of the barriers but for simplicity they are not depicted here. All our samples display a behaviour explained by case a) except the X=0.18 sample (small clusters) which displays a case c) behaviour.

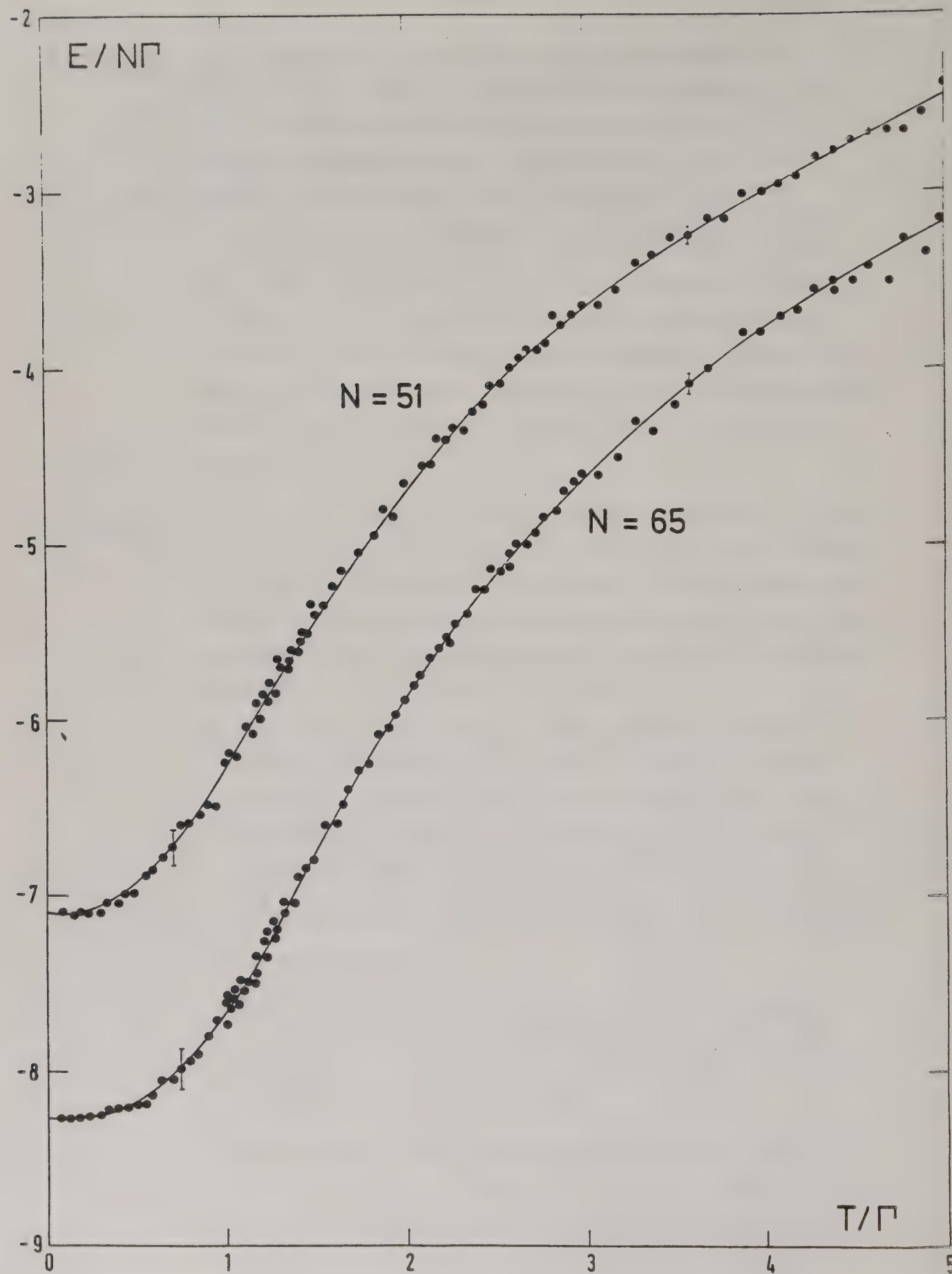

Figure 1

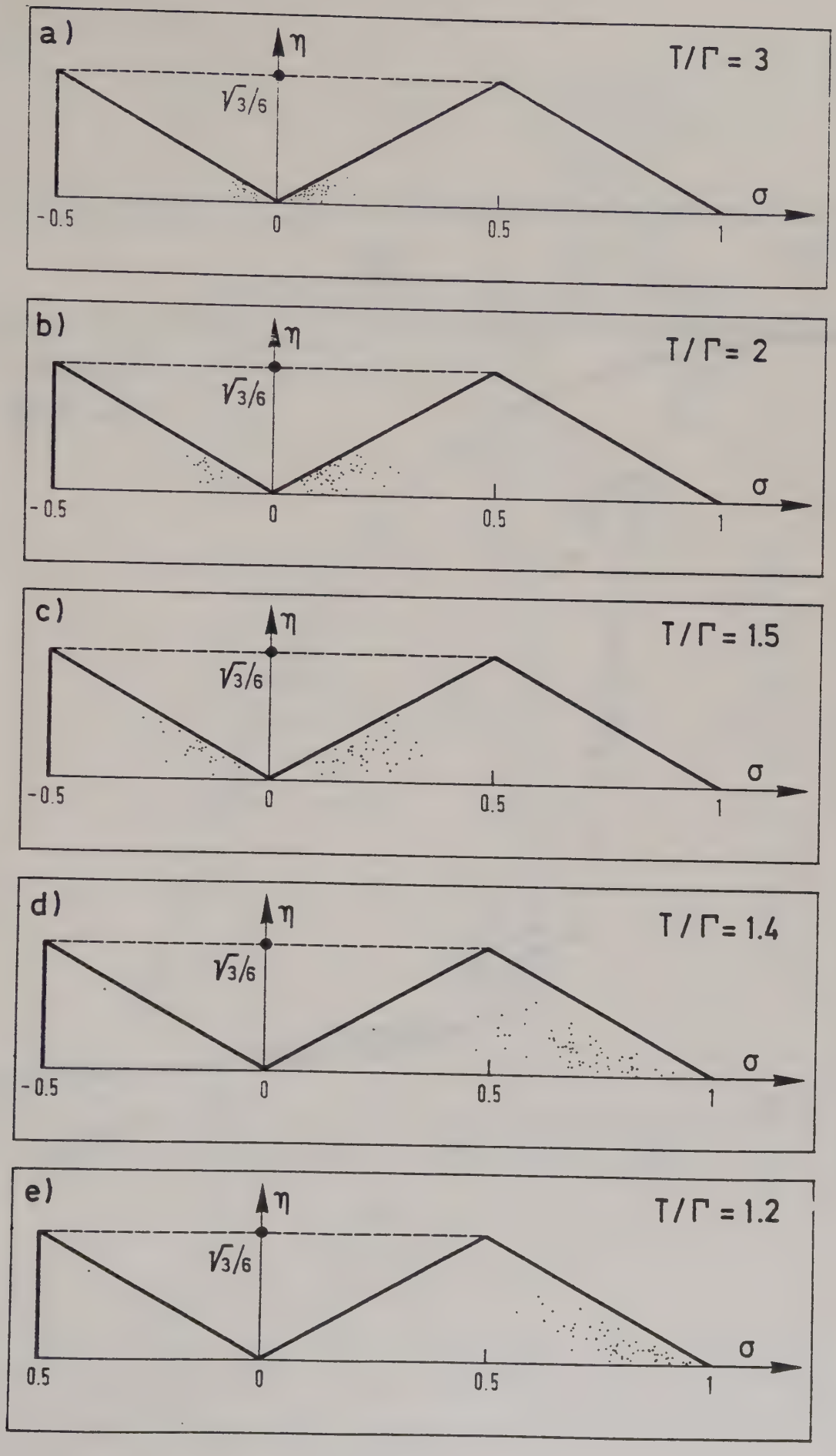
a)
η
T/Γ = 3
√3/6
σ
-0.5
0
0.5
1
b)
η
T/Γ = 2
√3/6
σ
-0.5
0
0.5
1
c)
η
T/Γ = 1.5
√3/6
σ
-0.5
0
0.5
1
d)
η
T/Γ = 1.4
√3/6
σ
-0.5
0
0.5
1
e)
η
T/Γ = 1.2
√3/6
σ
0.5
0
0.5
1

Figure 2

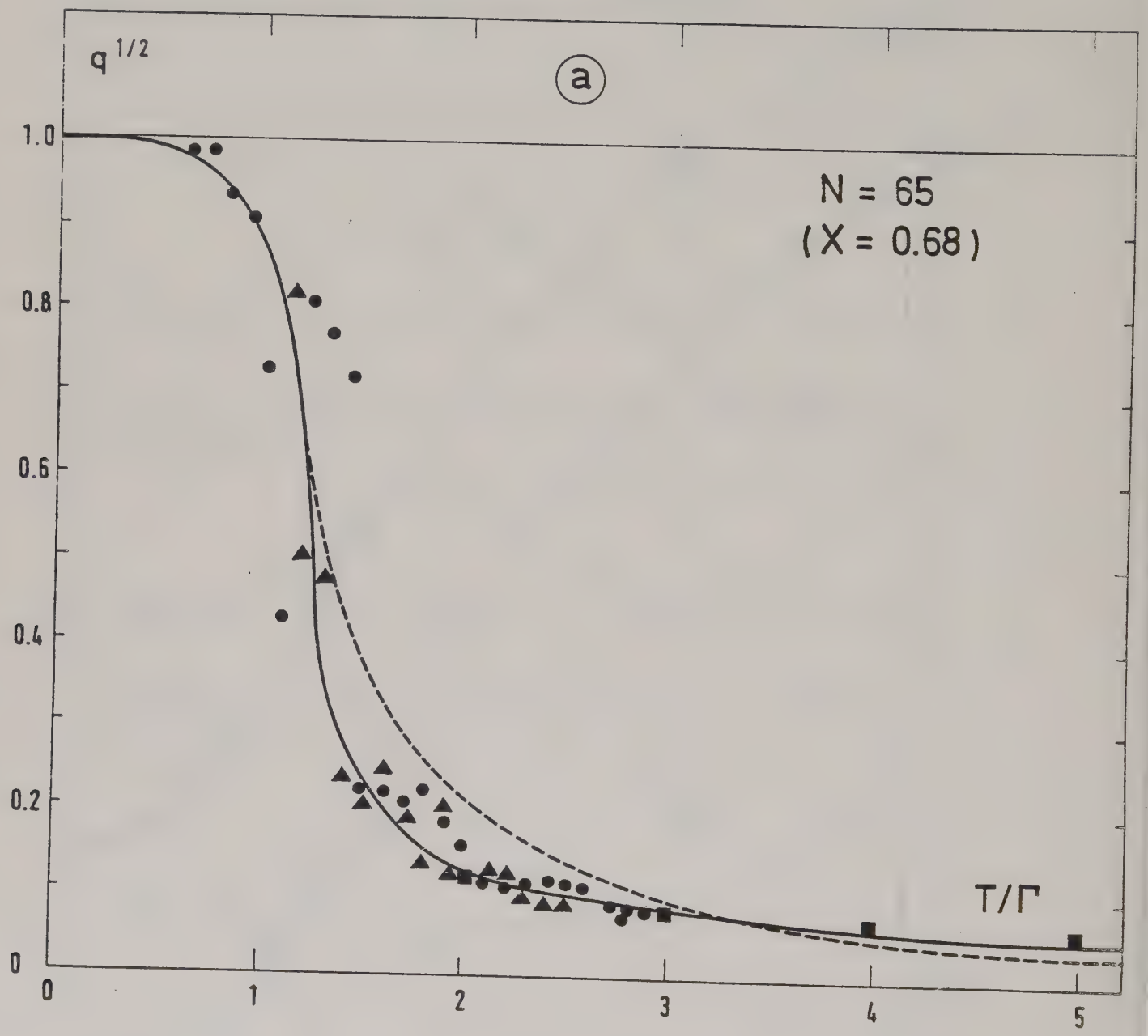

Figure 3a

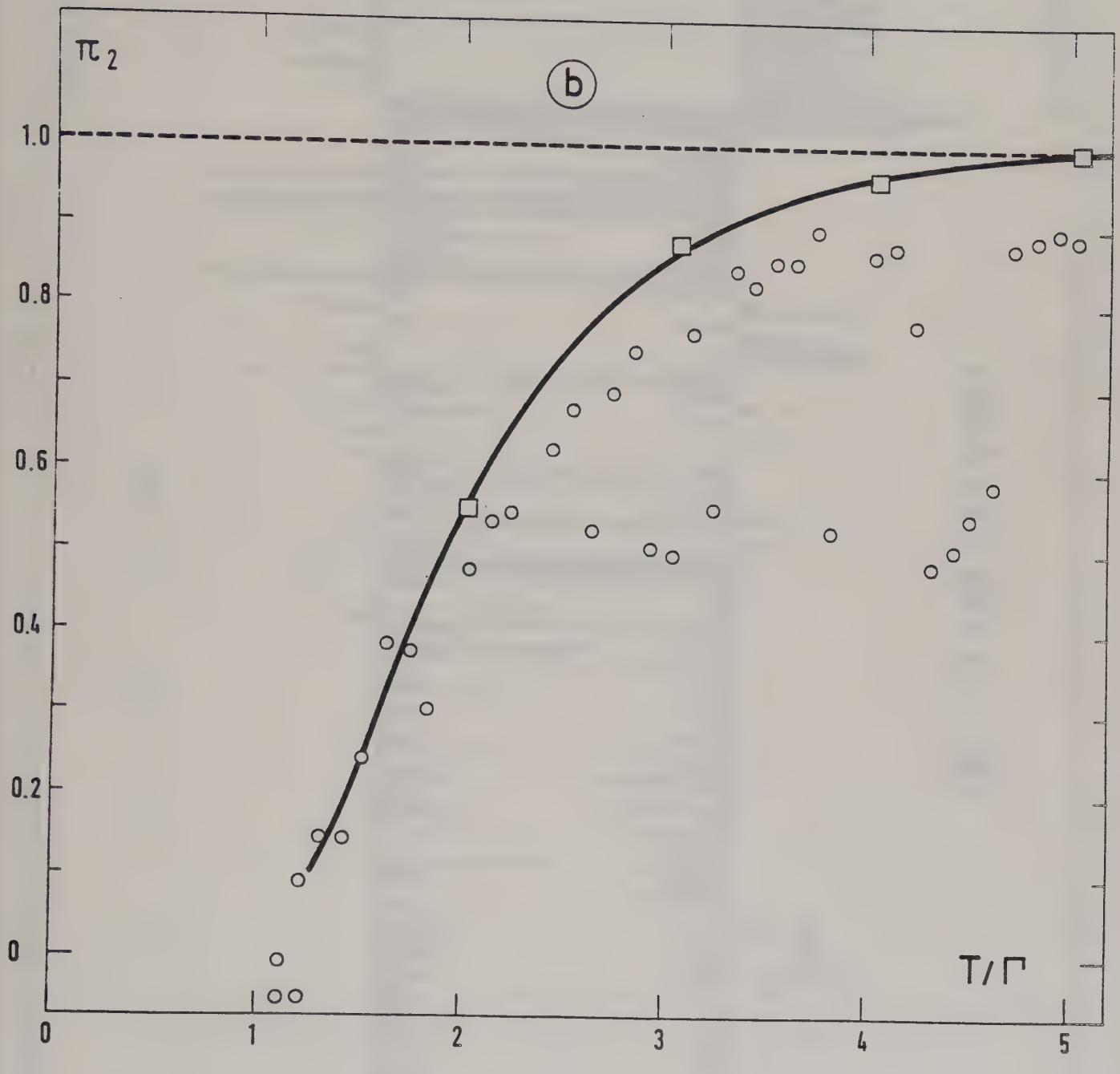

Figure 3b

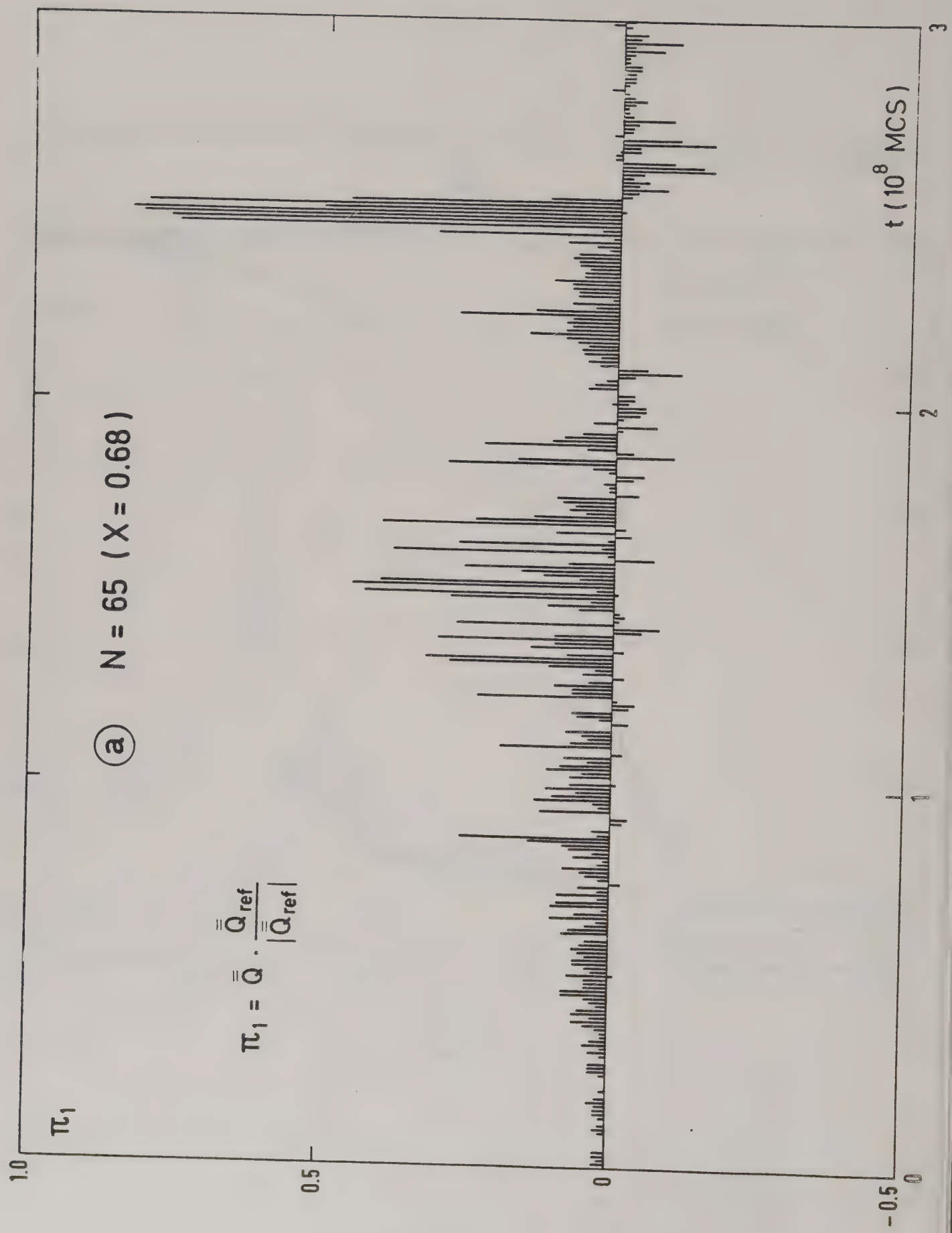
a
N = 65 (X = 0.68)
$\pi_1 = \bar{Q} \cdot \frac{\bar{Q}_{ref}}{|\bar{Q}_{ref}|}$
π_1
1.0
0.5
0
-0.5
0
1
2
3
t (10^8 MCS)

Figure 4a

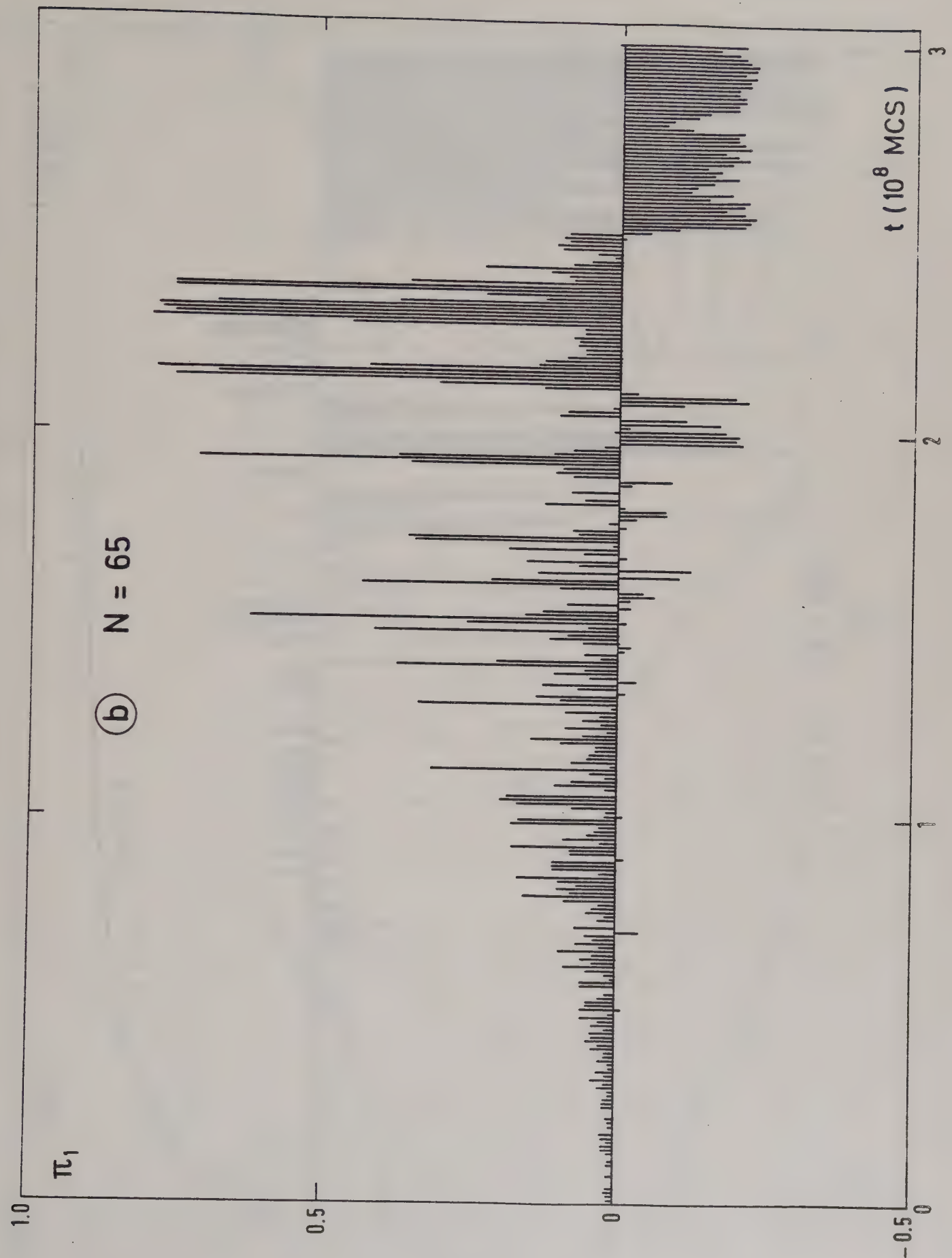

Figure 4b

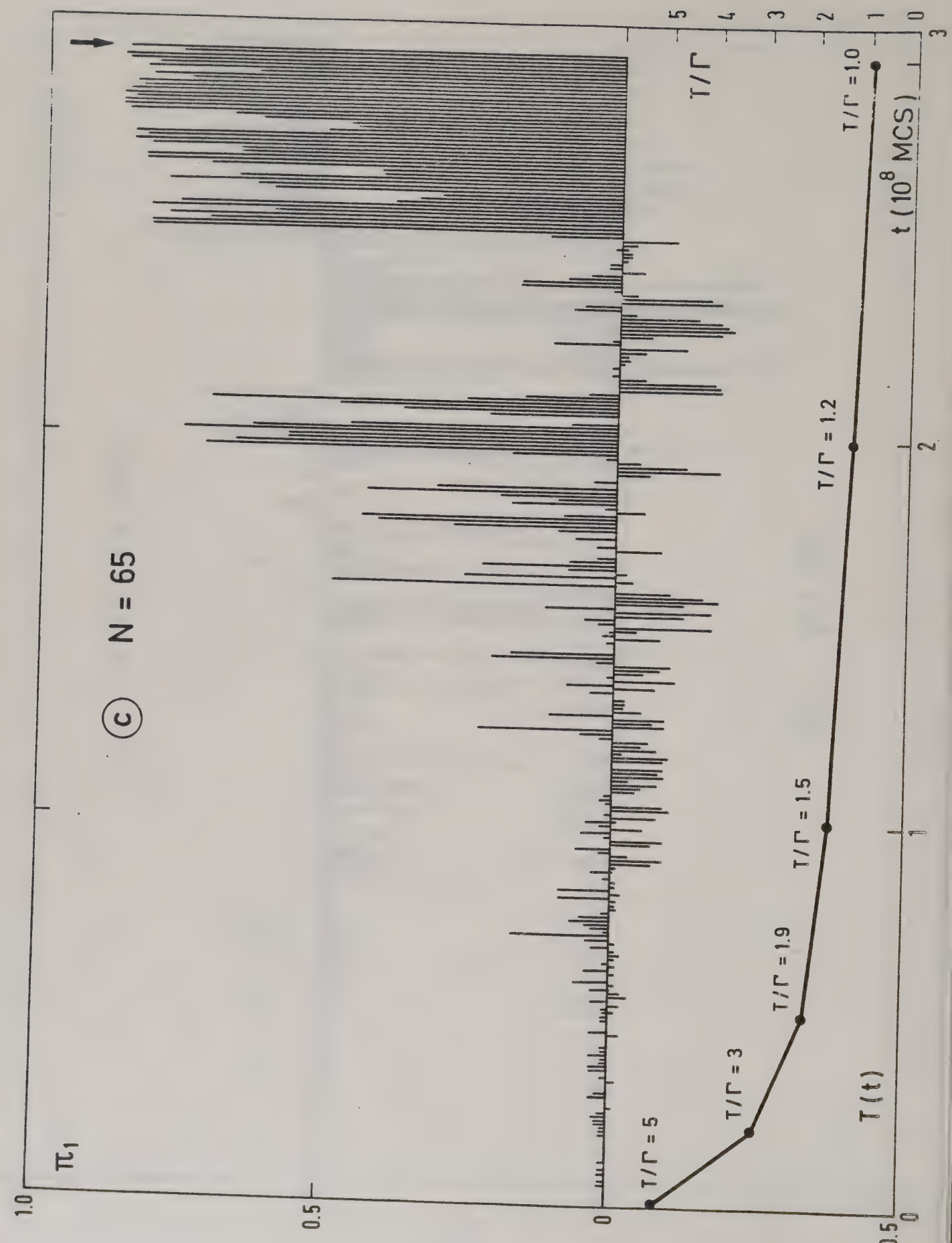
c
N = 65
π_1
1.0
0.5
0
-0.5
T/Γ
5
4
3
2
1
0
t (10^8 MCS)
3
2
1
0
T(t)
T/Γ = 5
T/Γ = 3
T/Γ = 1.9
T/Γ = 1.5
T/Γ = 1.2
T/Γ = 1.0

Figure 4c

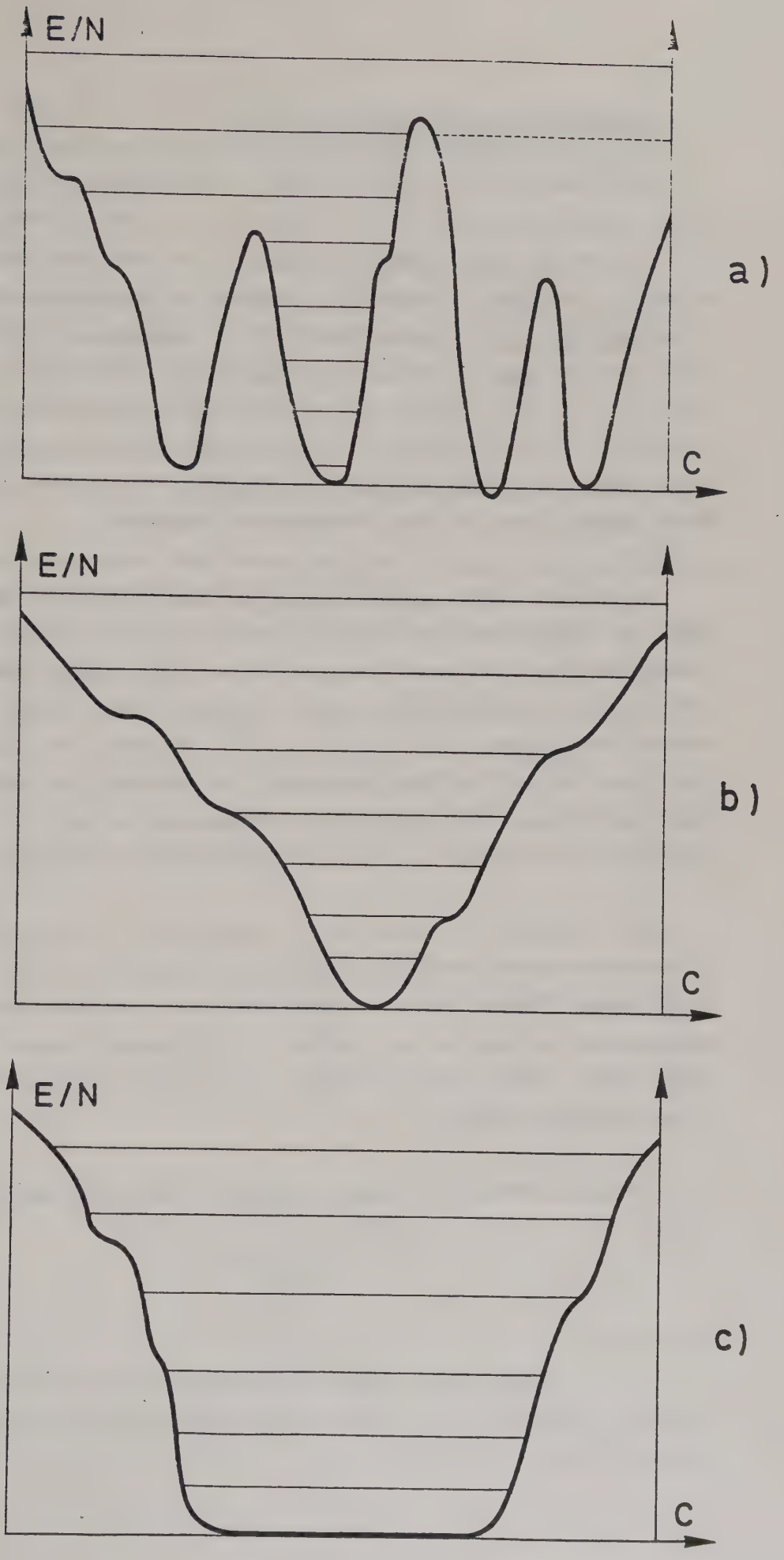

Figure 5

2. LA COMPARAISON EXPERIENCE/SIMULATION

Cette comparaison, abordée dans la conclusion de l'article précédent, appelle quelques commentaires. Il faut tout d'abord préciser la valeur de la constante Γ qui fixe l'échelle des températures. Nous pensons qu'une valeur raisonnable s'obtient en ajustant la température de transition orientationnelle de l'azote pur T_c=36.5K à celle que l'on trouve pour le réseau cubique cfc sans désordre $(T_c/\Gamma) = 3.4 \pm 0.1$* : on obtient alors $\Gamma = 10.7 \pm 1$K, valeur par ailleurs proche de celle estimée pour l'azote $\Gamma \simeq 9.7$K (cf partie B). On modélise ainsi les mélanges azote argon par un système "effectif" de quadrupoles purement classiques avec interactions limitées aux premiers voisins.

On constate alors que, bien que les quadrupolarisations obtenues dans les simulations numériques ne soient pas des valeurs à l'équilibre thermodynamique, elles se comparent mieux que qualitativement à celles déterminées expérimentalement pour la même concentration. La figure F1 montre ainsi comment les valeurs de $q^{1/2}$ obtenues lors des simulations (cf figure 3a de l'article précédent) se comparent aux valeurs observées expérimentalement (on notera que la détermination de $q^{1/2}$ n'est pas affectée par la présence de quadrupolarisations non-axiales).

Pour apprécier la portée de la comparaison, il faut aussi évaluer la correspondance entre le nombre de pas Monte Carlo d'une simulation et le temps d'évolution du système réel que l'on modélise. Cette correspondance ne peut en fait qu'être grossièrement évaluée, la dynamique Monte Carlo n'étant pas la dynamique réelle du système. Nous proposons l'équivalence suivante :

$$1 \text{ PMC par molécule} \equiv \text{temps typique de réorientation d'une molécule} \sim 1/\nu_{\substack{\text{libronique} \\ N_2 \text{ pur}}} \sim 10^{-9}\text{s} \quad .$$

---

* Cette valeur diffère légèrement de la valeur trouvée par Mandell (cf partie B) en raison de la limitation des interactions aux premiers voisins.

On peut alors évaluer à 10^{-5}s la durée "effective" des simulations de 5.10^{6}PMC pour N=65 molécules qui ont servi à déterminer la zone hachurée dans la figure F1.

Le phénomène de "gel" des orientations moléculaires que l'on observe dans les mélanges (N_2-Ar) sur une échelle de temps dépassant les 100s est donc l'équivalent de ce que l'on trouve pour un petit échantillon par simulation Monte Carlo au bout d'un temps effectif de simulation relativement bref.

Comment ce phénomène s'extrapole-t-il aux grands échantillons et aux temps longs ? La croissance importante temps caractéristiques d'évolution que nous avons observéeen doublant la taille de l'échantillon ne donne qu'une idée de la difficulté du problème.

II. LE SYSTEME SANS DESORDRE

1) Réseau cfc

La figure F2 montre les résultats d'une simulation portant sur 108 quadrupoles. On observe l'apparition à $T_c/\Gamma = 3.4 \pm 0.1$ d'une phase ordonnée à longue distance formée d'un domaine de structure Pa3 à quatre sous réseaux. Cette transition du premier ordre est bien comprise, mais il n'en existe pas de théorie complètement satisfaisante en raison notamment des difficultés de traitement que présentent les corrélations orientationnelles dans la phase désordonnée.

2) Réseau hc

Bien qu'étant un problème d'école, le problème de l'ordre orientationnel d'un système de quadrupoles sur réseau hexagonal compact est une étape nécessaire dans la compréhension des systèmes désordonnés sur le même réseau. La théorie de champ moyen de James [J68] prévoit un état fondamental de symétrie $Pca2_1$ et l'existence d'une cascade de trois transitions orientationnelles avec des structures intermédiaires de symétries $P2_1/c$ et Pnma. Les premières simulations numériques effectuées [M74] n'ont pas montré de telles transitions mais ont indiqué la présence d'un ordre orientationnel partiel à basse température. Ce problème a depuis fait l'objet d'études plus approfondies en raison de l'intérêt suscité par les verres de quadrupoles. Les résultats que nous avons obtenus sont en accord avec ceux de M. Klenin [K82] : nous présentons ici les conclusions de ces études.

La figure F3 montre l'évolution de l'énergie et de la projection π_1 sur l'état orientationnel obtenu en fin d'évolution au cours d'un refroidissement. La courbe d'énergie ne montre pas de courbe brusque comme dans le cas du réseau cfc, mais seulement un point d'inflexion correspondant à un pic dans la chaleur spécifique centré à $T/\Gamma = 2.7$. La projection π_1 présente dans la même zone en température $2.5 < T/\Gamma < 3$ d'importantes fluctuations qui traduisent "l'hésitation" du système dans le choix de l'une de ses structures possibles. L'état orientationnel choisi par le système n'est pas un état régulier de symétrie $Pca2_1$, mais contient des défauts. Les différents plans perpendiculaires à l'axe $\hat{c}$ présentent un ordre de type chevron (voir figure F4), la direction

des chevrons étant la même pour tous les plans, mais l'empilement de ces plans ne s'effectuant pas de façon périodique comme l'exigerait la symétrie $Pca2_1$ (le défaut d'énergie qu'entraîne une telle irrégularité est très faible).

Ce désordre résiduel peut être éliminé par un longrecuit de l'échantillon à la température d'ordre [K82] et est donc un phénomène hors d'équilibre. Il est néanmoins révélateur de la pathologie particulière que présentent des quadrupoles sur un réseau hc. On comprend alors mieux pourquoi le désordre perturbe si facilement cette structure si difficile à nucléer et pourquoi les mélanges (N_2-Ar) ne présentent pas d'ordre à longue distance en phase hexagonale.

Ces résultats soulèvent une fois encore le problème de la comparaison entre l'échelle de temps des simulations numériques sur de petits échantillons et celle du monde physique. Cette question qui dépasse largement le cadre des quadrupoles semble être cruciale dans le cas des systèmes frustrés désordonnés. Certains pensent ainsi que les simulations numériques "trop puissantes" du problème verre de spin effectuées depuis 1975, qui ne montrent pas de transition nette, ne correspondent tout simplement plus à l'échelle de temps des expériences !

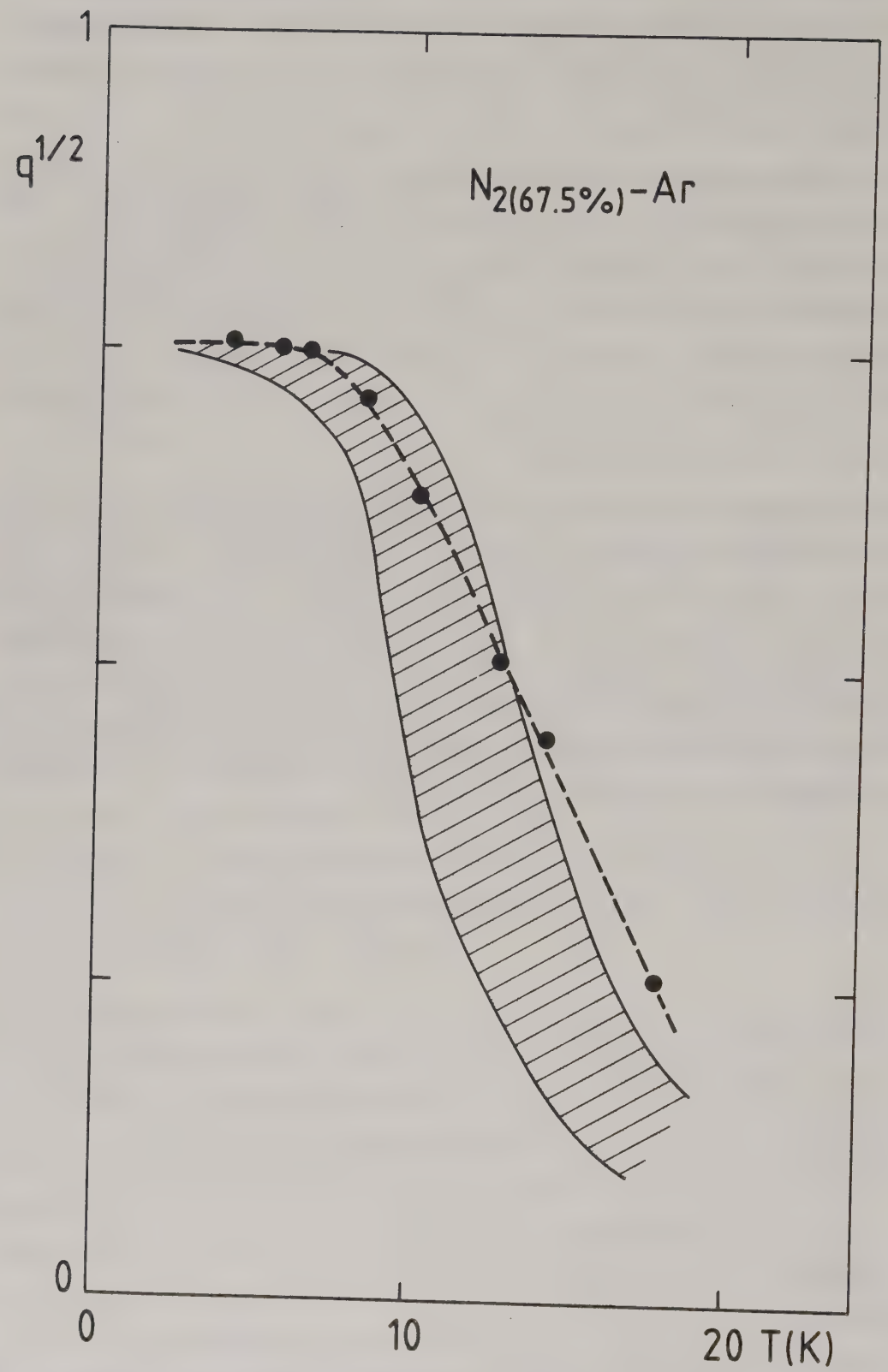

Figure F1 - Cercles pleins : évolution de l'écart standard $q^{1/2}$ des quadrupolarisations dans ($N_{2(67.5\%)}$ - Ar) déduite des spectres RMN. En grisé : zone de répartition des valeurs de $q^{1/2}$ obtenues lors de simulations numériques portant sur N=65 molécules réparties aléatoirement sur 96 sites (X ≃ 68%) après 10^6-10^7 pas Monte Carlo. Ces valeurs ont été affectées d'un coefficient de renormalisation qui prend en compte la localisation orientationnelle incomplète des molécules d'azote à T=0K.

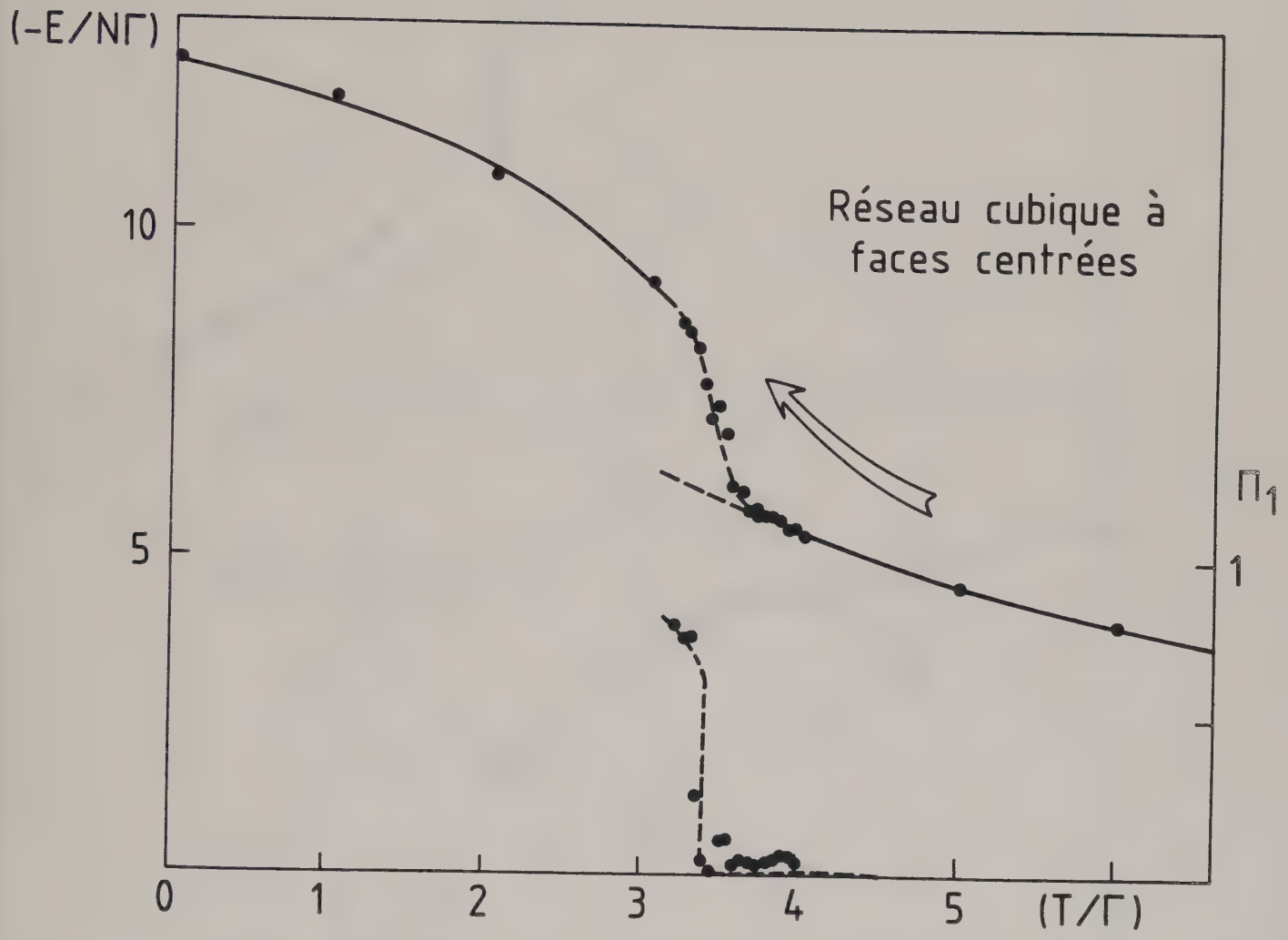

Figure F2 - Evolution Monte Carlo d'un système de quadrupoles en interaction sur un réseau cfc au cours d'un refroidissement (10^6 pas MC par point). La courbe d'énergie montre un accident marqué. On observe la nucléation d'un domaine de structure Pa3 à la transition (transition du 1er ordre) comme l'indique l'évolution de la projection π_1 sur l'état fondamental Pa3 choisi parmi les huit possibles par le système.

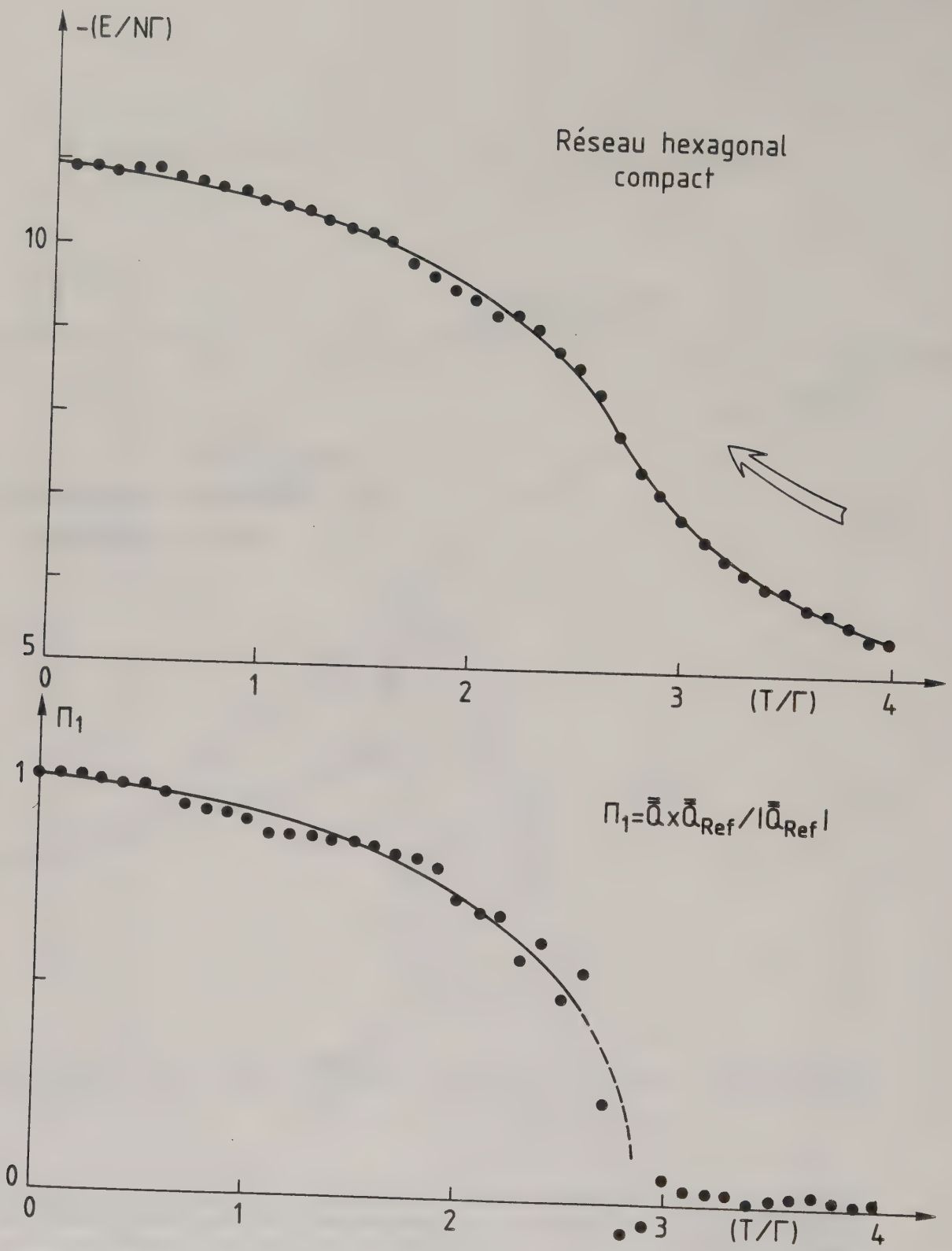

Figure F3 - Evolution Monte Carlo d'un système de quadrupoles en interaction sur un réseau hc au cours d'un refroidissement (10^6 pas par point). La courbe d'énergie ne montre qu'un point d'inflexion vers $T/\Gamma = 2.7$. La projection π_1 sur l'état final à $T/\Gamma = 0$ montre d'importantes fluctuations dans la zone $2.5<T/\Gamma<3$.

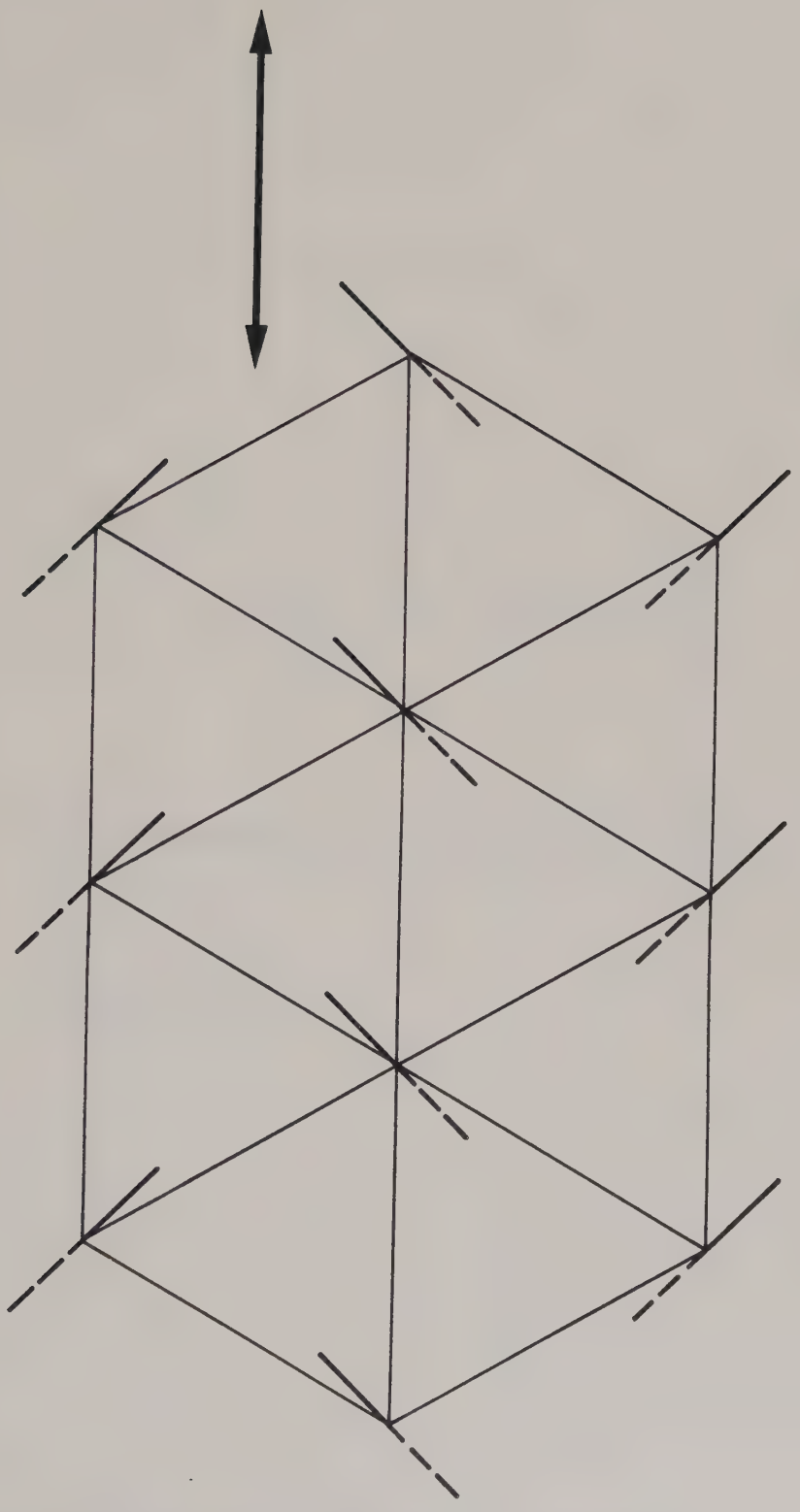

Figure F4 - Orientations des quadrupoles d'un plan perpendiculaire à l'axe ĉ dans la structure obtenue à basse température. Les pointillés signalent les côtés des tiges en-dessous du plan. Les tiges sont toutes inclinées du même angle par rapport à l'axe ĉ. La direction des chevrons est indiquée par la double flèche.

PARTIE G : TECHNIQUES EXPERIMENTALES

I - FONCTIONNEMENT DE LA CELLULE EXPERIMENTALE

II - TECHNIQUES RMN

Nous présentons dans cette partie l'appareillage expérimental et son mode de fonctionnement dans ses grandes lignes pour l'ensemble, et avec plus de détails pour quelques points, soit spécifiques aux expériences effectuées, soit au contraire d'un intérêt général.

I. FONCTIONNEMENT DE LA CELLULE EXPERIMENTALE

Compte-tenu de la valeur relativement élevée de la température de transition orientationnelle dans l'azote solide pur (T=35.6K), nous avons réalisé une cellule expérimentale destinée à fonctionner au-dessus de T=4.2K (1.2K éventuellement) dans un cryostat conventionnel. Cette cellule (figure G1) permet de préparer dans une bobine RMN un échantillon solide sous forme de poudre d'azote, ou d'azote-argon, et d'étudier la RMN des noyaux $^{15}N_2$ à toute température de 4. 2K à 60K. Le champ magnétique est fourni par une bobine supraconductrice placée autour de la cellule.

1. LA PREPARATION DES ECHANTILLONS

La préparation des échantillons gazeux s'effectue à l'aide d'un banc de servitude utilisant en particulier un piège à charbon actif (60cc) baignant dans l'azote liquide. Un tel piège, qui peut adsorber plusieurs litres d'azote ou d'argon en quelques minutes avec une pression résiduelle inférieure à 10^{-2}T, permet d'introduire successivement les composants d'un mélange gazeux dans le même volume de référence. La valeur de la concentration (obtenue avec une précision de l'ordre de 1%) est déduite de la mesure des pressions des composants dans ce volume à température donnée. Quelques cycles d'adsorption du mélange dans le piège donnent alors un mélange homogène. Un peu d'oxygène est ajouté (500 ppm typiquement) pour obtenir un échantillon dont le temps de relaxation longitudinal T_1 est de l'ordre de 5 à 10s à 4K.

La condensation sur les cheveux de cuivre s'effectue en introduisant successivement de petites quantités de gaz dans la cellule préchauffée à T ≃ 60K, tout en surveillant pression et température pour éviter le passage par une phase liquide qui donnerait deux solides de compositions

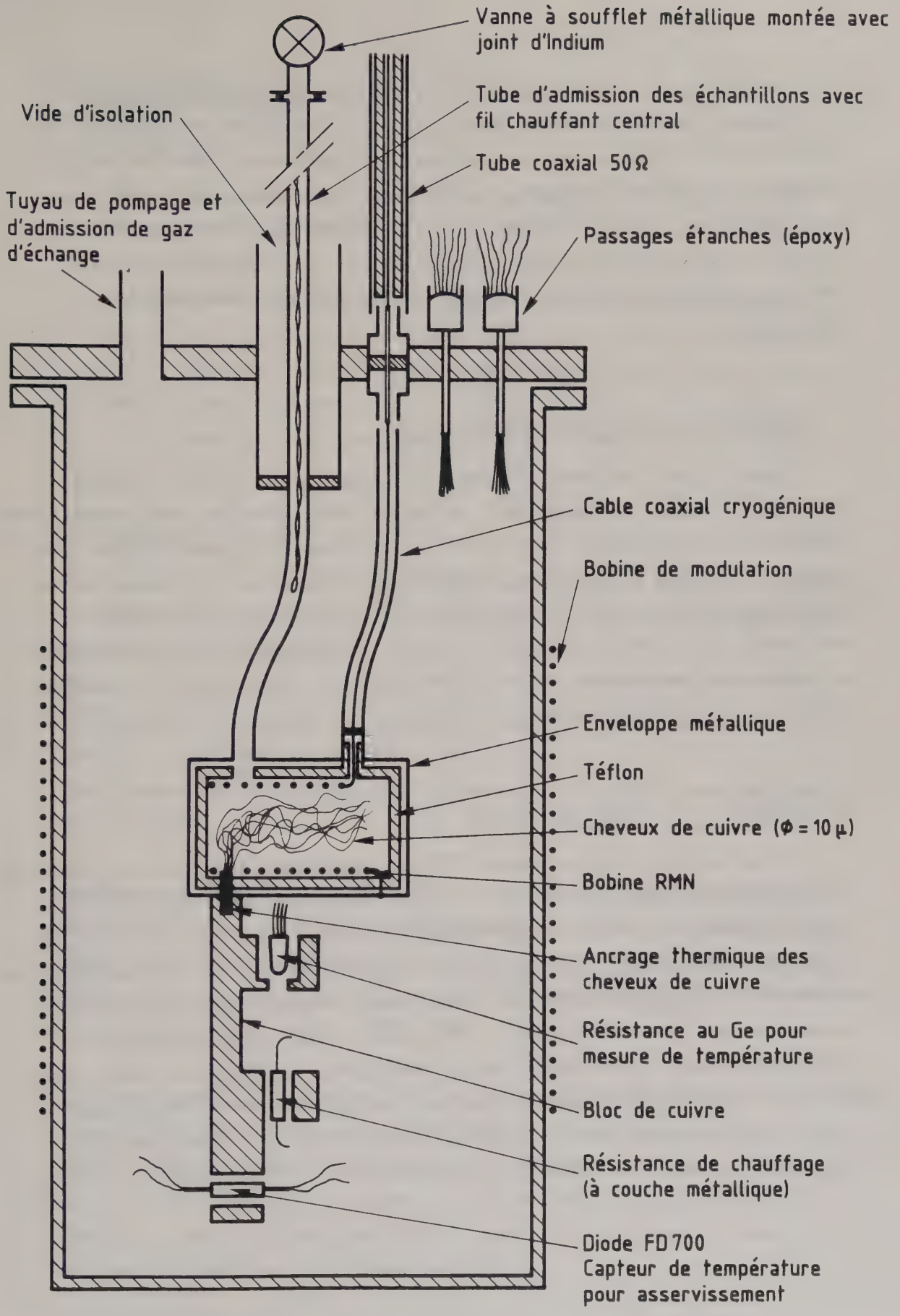

FIG. G1 - SCHEMA DE LA CELLULE EXPERIMENTALE

différentes en se refroidissant. Les résultats que nous avons obtenus ne dépendant pas des diverses modalités de préparation des échantillons essayées, nous pensons que ces derniers correspondent bien à un solide homogène sous forme de poudre. Un bon vide d'isolation autour du tube de descente est nécessaire pour éviter un piégeage préférentiel de l'argon avant son arrivée dans la cellule. Le fil chauffant central permet d'effectuer le remplissage de la cellule sans bouchage de ce même tube.

2. THERMALISATION DE L'ECHANTILLON SOLIDE

Outre le fait de favoriser la réalisation d'une poudre homogène, les cheveux de cuivre permettent une bonne thermalisation des échantillons en dépit de la mauvaise conductivité thermique de l'azote solide. Ces cheveux de cuivre sont ancrés thermiquement à un bloc de cuivre dont la température est régulée. Le capteur utilisé pour cet asservissement est une simple diode FD700 qui opère de façon satisfaisante* de 4.2K à 80K. La mesure de température est effectuée avec une résistance au germanium placée près de l'échantillon.

3. HOMOGENEITE DU CHAMP MAGNETIQUE

La cellule ne comprend aucun élément magnétique au voisinage immédiat de l'échantillon (le passage RF est monté ainsi sur tourelle,...). Nous avons constaté malgré ces précautions la présence d'un fort gradient de champ, provenant en fait d'une détérioration de la bobine supraconductrice utilisée. La réalisation de deux enroulements annexes de compensation traversés par des courants réglables a permis de réduire ce gradient, et d'atteindre ainsi une homogénéité de champ meilleure que 100-200mG (selon les jours !) dans la gamme de champ envisagée (5 à 10kG). Un réglage précis des courants de compensation s'effectue en optimisant la durée du signal d'induction libre d'un échantillon de $^{14}N_2$ liquide à T ≈ 70K.

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* La présence d'une forte capacité (1μF) en parallèle est nécessaire pour supprimer le très fort bruit HF que fournit la diode.

II. TECHNIQUES RMN

1. SPECTRES CW

Nous avons obtenu des spectres CW en balyage de champ avec soit un oscillateur de Robinson [DVS77] soit un Q-mètre en montage standard.

Nous avons utilisé un accumulateur multi-canaux pour atteindre un rapport signal/bruit satisfaisant (500 accumulations typiquement). Le spectre résultant était ensuite traité numériquement (soustraction de ligne de base, lissage, normalisation) sorti de façon graphique et éventuellement mis en mémoire sur cassette (HP).

2. TECHNIQUES D'IMPULSIONS

Le principe de fonctionnement du spectromètre à impulsions que nous avons utilisé est indiqué sur les figures G2 et G3. Nous en commentons ci-dessous les éléments.

Générateur RF : générateur synthétisé Adret de très haute stabilité en fréquence. (Une dérive inférieure à 0.1 $Hz.s^{-1}$ est nécessaire lorsque l'on observe des échos avec une séparation entre impulsions de l'ordre de la seconde).

Générateur d'impulsions : Les différents temps (durées, délais) sont réalisés à partir de circuits analogiques. La gestion des impulsions à partir d'un micro-ordinateur est maintenant une solution plus élégante, quoique moins souple d'emploi. Le circuit de synchronisation est nésessaire pour avoir des impulsions parfaitement reproductibles.

Amplificateur RF de puissance : C'est un amplificateur large bande 1-20MHz à quatre étages. Les étages 3 et 4 travaillent en classe C. Le dernier étage utilise le transistor de puissance MRF428A qui s'est avéré extrêmement fiable ainsi que des auto-transformateurs à tore pour adapter l'impédance de sortie du transistor (de l'ordre de quelques ohms) à celle du circuit résonnant (de l'ordre de 50Ω).

Spectromètre RMN (figure G3) : La transmission des impulsions RF à la bobine RMN s'effectue grâce au circuit accordé (L_s,C_s) qui présente à

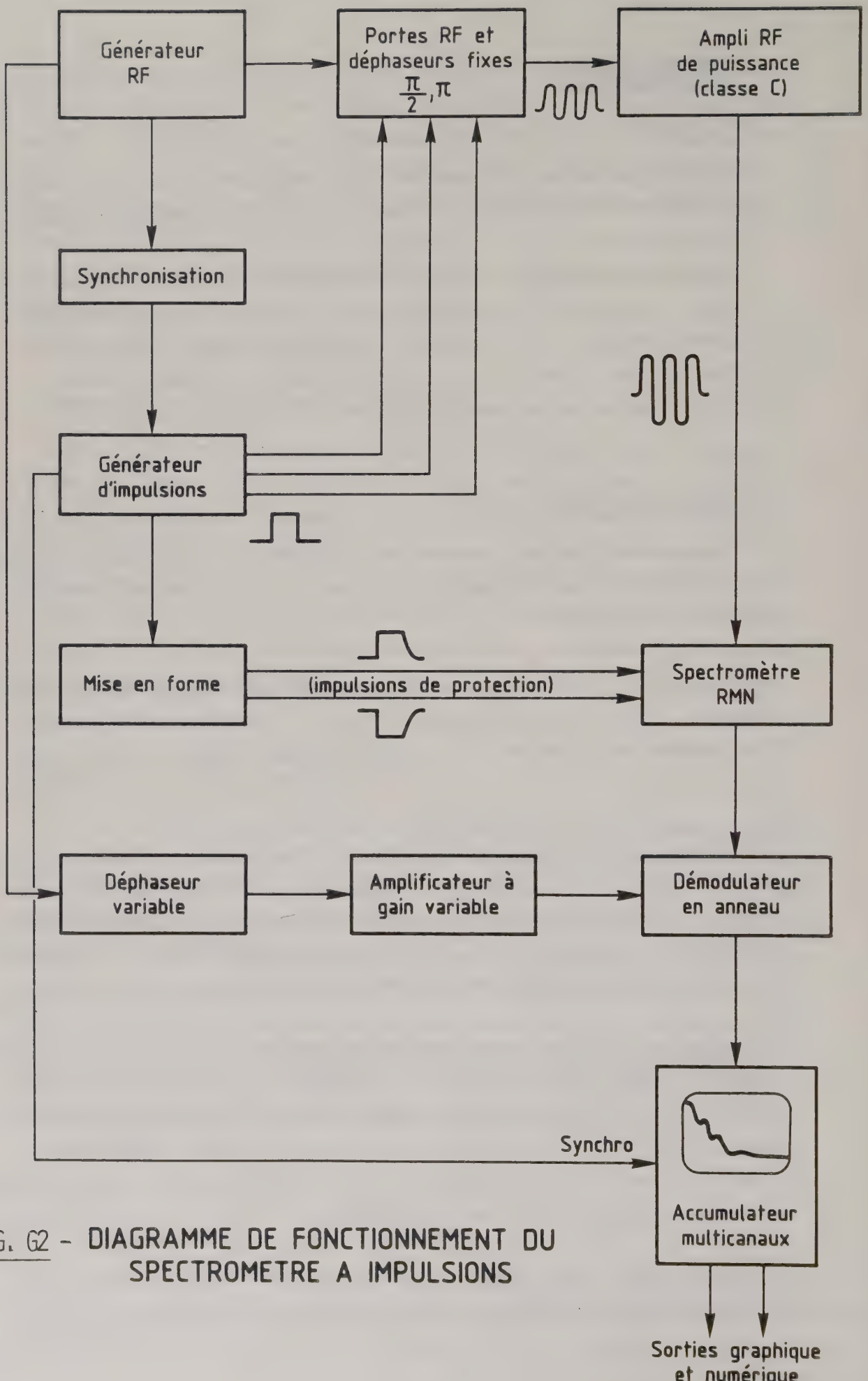

FIG. G2 - DIAGRAMME DE FONCTIONNEMENT DU SPECTROMETRE A IMPULSIONS

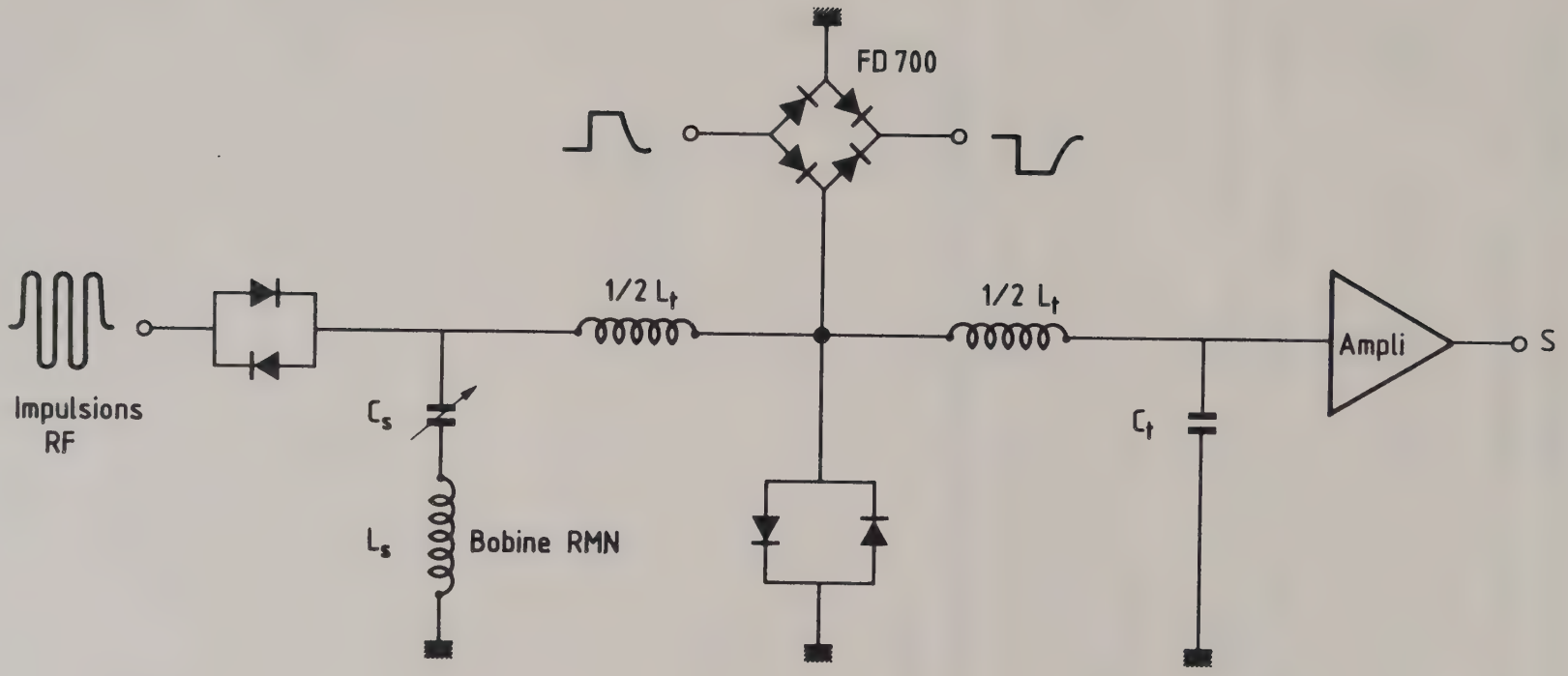

FIG. 63 - SCHEMA DE PRINCIPE DE LA TRANSMISSION DES IMPULSIONS ET DE LA RECEPTION DU SIGNAL RMN

résonance une impédance adaptée à celle de l'amplificateur de puissance.

La réception du signal RMN utilise un amplificateur large bande via le circuit adapteur d'impédance (L_t,C_t).

L'utilisation d'un système de protection de l'amplificateur pendant les impulsions est nécessaire lorsque l'on désire observer le signal avec un temps mort aussi réduit que possible. N. Sullivan a depuis développé un spectromètre RMN mettant en oeuvres plusieurs circuits de ce type et une *contre réaction active* pour obtenir un temps mort très court [SDNV82].

Détection du signal : Le signal est détecté à l'aide d'un démodulateur en anneau (HP) dont la référence est alimentée par le générateur RF via un déphaseur ajustable. Nous avons utilisé un accumulateur rapide (Nicolet 1070) pour atteindre un rapport signal/bruit suffisant. La sortie des données s'effectuait essentiellement par lecture directe du contenu des canaux intéressants.

PARTIE : H

CONCLUSION

En résumé :

Nous avons développé des méthodes RMN d'investigation de l'état orientationnel de molécules du type hydrogène, azote. En appliquant ces méthodes à l'étude des mélanges solides azote-argon nous avons mis en évidence un verre orientationnel, caractérisé par des orientations des molécules d'azote gelées de façon aléatoire.

RMN ET ORDRE ORIENTATIONNEL

Notre étude a porté sur :

- L'analyse quantitative des formes de raie RMN pour en extraire la distribution des quadrupolarisations des molécules.

- Les échos solides obtenus après une séquence de deux impulsions RF ; nous avons interprété leurs lois d'amortissement et nous les avons utilisés pour étudier l'ordre orientationnel dans l'azote pur.

- Les échos stimulés obtenus après une séquence de trois impulsions RF. Nous avons montré comment ces échos permettent de détecter des mouvements de rotation des molécules extrêmement lents.

- L'analyse de la relaxation longitudinale pour des molécules ordonnées orientationnellement.

UN VERRE ORIENTATIONNEL DANS LES MELANGES AZOTE-ARGON

Nous avons observé dans les mélanges azote-argon en phase hexagonale l'existence à basse température d'un verre orientationnel. Ce verre est l'analogue pour les orientations des molécules d'un verre conventionnel pour les positions des atomes ou d'un verre de spin pour les moments magnétiques : les molécules adoptent des orientations aléatoires fixes au cours temps et sans ordre à longue distance.

Les modalités d'apparition de l'ordre vitreux dans les mélanges azote-argon sont par contre très particulières : lorsque l'on abaisse la température, la localisation orientationnelle des molécules croît

progressivement jusqu'à saturation quasi complète et n'évolue plus ensuite. Cette localisation s'opère sans donner lieu à des mouvements lents et à des phénomènes d'hystérésis notables. La simulation numérique d'un système de quadrupoles classiques en interaction que nous avons réalisée indique cependant que le verre orientationnel résulte d'un phénomène coopératif.

Ce comportement inusité des verres de quadrupoles semble très lié à certains aspects spécifiques de ces systèmes, et notamment à leur absence de symétrie globale.* Les systèmes désordonnés de quadrupoles occupent une place originale parmi les systèmes qui présentent un ordre de type vitreux.

* Il faut souligner ici que la nature des symétries présentes semble de même influer de façon importante les propriétés des verres de spin.

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Des mesures de chaleur spécifique des mélanges N_2-Ar avaient déjà été effectuées par Pace, Smith et Jepson (J. Chem. Phys. 50 (1969) 312) et par Chauzov, Manzhelii et Freiman (Soviet Physics, Solid State 11 (1970) 2947).

RESUME

Nous présentons une étude RMN des mélanges solides azote-argon. Dans ce système, les molécules d'azote peuvent être considérées comme des rotateurs classiques répartis au hasard sur un réseau et couplés par des interactions anisotropes, de courte portée, du type quadrupole-quadrupole. Nous avons étudié à l'aide de méthodes RMN originales l'ordre orientationnel dans ce système, qui combine de façon particulière la frustration et le désordre. Nous avons notamment mis en évidence l'existence à basse température d'un verre orientationnel, dans lequel les molécules d'azote adoptent des orientations aléatoires fixes dans le temps.

Mots-clefs : solides moléculaires, ordre orientationnel, interactions quadrupolaires frustration, désordre, verre, RMN pulsée, échos.

ABSTRACT

We present an NMR study of nitrogen-argon solid mixtures, in which the N_2 molecules can be considered as almost classical rotators randomly distributed on a lattice. The orientational ordering of the molecules due to their short range highly anisotropic interactions presents an original case-study of the combined effects of frustration and disorder. Using original NMR methods, we have in particular shown the existence at low temperature of an orientational glass regime, characterised by random frozen-in orientations of the N_2 molecules.

Key-words : molecular solids, orientational ordering, quadrupolar interactions, frustration, disorder, glass, pulsed NMR, echoes.